LIGAND DISPLACEMENT REACTIONS OF BINUCLEAR RUTHENIUM COMPLEXES

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To Pauline, Vincent and Peter,

and to my Mother and Father.

DECLARATION

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results presented have already been published.

(Thomas Easton)

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ABSTRACT

Chapter 1 states the main objective of this work, the catalytic conversion of ethene to vinyl chloride using triple-halide-bridged binuclear ruthenium complexes, and emphasises the industrial significance of such a process. A brief account of relevant ruthenium chemistry is also given.

Chapter 2 describes a new synthetic route to the complex $Ru_2Cl_4(PMe_2Ph)_5$ involving photolysis of monomeric species. This and related complexes are used to prepare novel cationic triple-halide-bridged binuclear ruthenium complexes with the general formula $[Ru_2X_3(L)(PR_3)_5]^+$ where L = alkene, alkyne and dinitrogen and X = Cl^- or Br^-. The ease of formation of these cationic complexes is dependent upon the nature of the tertiary phosphine ligands and a general trend has been identified. Electrochemical studies on the C_2H_4 and N_2 complexes are described. The former complex has been shown to undergo alkene displacement rather than modification in the presence of a variety of nucleophiles.

Chapter 3 describes the synthesis of the unusual asymmetric double-chloride-bridged binuclear complexes $(Et_2PhP)(L)_2ClRuCl_2RuCl(PEt_2Ph)_3$ (L = C_2H_4, PhC≡CH) *via* chemical reduction of the mixed-valence complex $Ru_2Cl_5(PEt_2Ph)_4$. Preliminary evidence is given for the slow conversion of ethene to ethanal in the bis-ethene complex in the presence of H_2O or OH^-.

Chapter 4 discusses the reactions of $RuCl_2(PPh_3)_3$ and $RuCl_2(CO)(PPh_3)_2dmf$ with the alkenyl tertiary phosphine $Ph_2P(CH_2)_2CH=CH_2$. In both cases the final products have been characterised by spectroscopic and X-ray structural analysis, and a stepwise ligand displacement pathway has been identified for $RuCl_2(CO)(PPh_3)_2dmf$. Attempted coupling reactions of the new alkenyl phosphine complexes are described. Triple-chloride-bridged binuclear complexes containing alkenyl phosphines, prepared using the chloride-abstracting technique covered in Chapter 2, are also described.

Chapter 5 is concerned with the unexpected reaction of $RuCl_2(CO)(PPh_3)_2dmf$ and phenylacetylene to give $RuCl_2(CO)_2(PPh_3)_2$ and toluene. A series of experiments is described which have allowed a tentative reaction pathway to be proposed for this reaction. Treatment of $RuCl_2(CO)_2(PPh_3)_2dmf$ with dimethylacetylenedicarboxylate is shown to be an effective route to the known complex $(Ph_3P)(CO)ClRuCl_3Ru(CO)(PPh_3)_2$.

Chapter 6 describes the synthesis of the novel heterotrimetallic complex $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ by reaction of $RuCl_2(PEtPh_2)_3$, $Ru_2Cl_4(PEtPh_2)_5$ or $[Ru_2Cl_3(PEtPh_2)_6]Cl$ with AgCl. Preparation of the nitrato complex $RuCl(O_2NO)(PEtPh_2)_3$ *via* $RuCl_2(PEtPh_2)_3$ and $Ag(PEtPh_2)_2NO_3$ is also discussed. X-ray structural analyses have been carried out on both complexes. Attempts to prepare novel fluoride/tertiary phosphine ruthenium(II) complexes are described.

CONTENTS

CHAPTER 4 Reactions of Monomeric and Binuclear Ruthenium(II) Complexes with Alkenyl Tertiary Phosphines

FIGURES

(N.B. Unless otherwise stated, ^{31}P and ^{1}H n.m.r. spectra were recorded at ambient temperature)

SCHEMES

TABLES

CHAPTER 1

INTRODUCTION

1.1. INDUSTRIAL BACKGROUND AND AIMS OF THIS WORK

The increase in the production of vinyl chloride, the principal monomer for poly (vinyl chloride) plastics which are used in vinyl flooring, phonograph records, shower curtains, car seat upholstery, pipe *etc.* is spectacular. Production in the United States has increased from 250 million lbs in 1950 (when it was declared a mature chemical commodity by many industrial economic forecasters), to over one billion lbs. in 1960, 3.5 billion lbs in 1970, and over 7 billion lbs in 1980.

During the early development of vinyl resins in the 1930's, vinyl chloride was produced *via* Hg(I) - catalysed addition of hydrogen chloride to ethyne (Equ. 1).

$$CH \equiv CH + HCl \xrightarrow{Hg_2Cl_2} CH_2 = CHCl \quad \ldots (1)$$

Later, a so-called "balanced" process was introduced in which 1,2-dichloroethane was produced by addition of chlorine to ethene. 1,2-dichloroethane could then be "cracked" to vinyl chloride and HCl (Equ. 2).

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl\text{-}CH_2Cl \longrightarrow CH_2CHCl + HCl \quad \ldots (2)$$

To make the process economic, the HCl was then employed to produce further vinyl chloride from ethyne (Equ. 1). Accordingly, at this time vinyl chloride was being produced

from chlorine, ethyne and ethene.

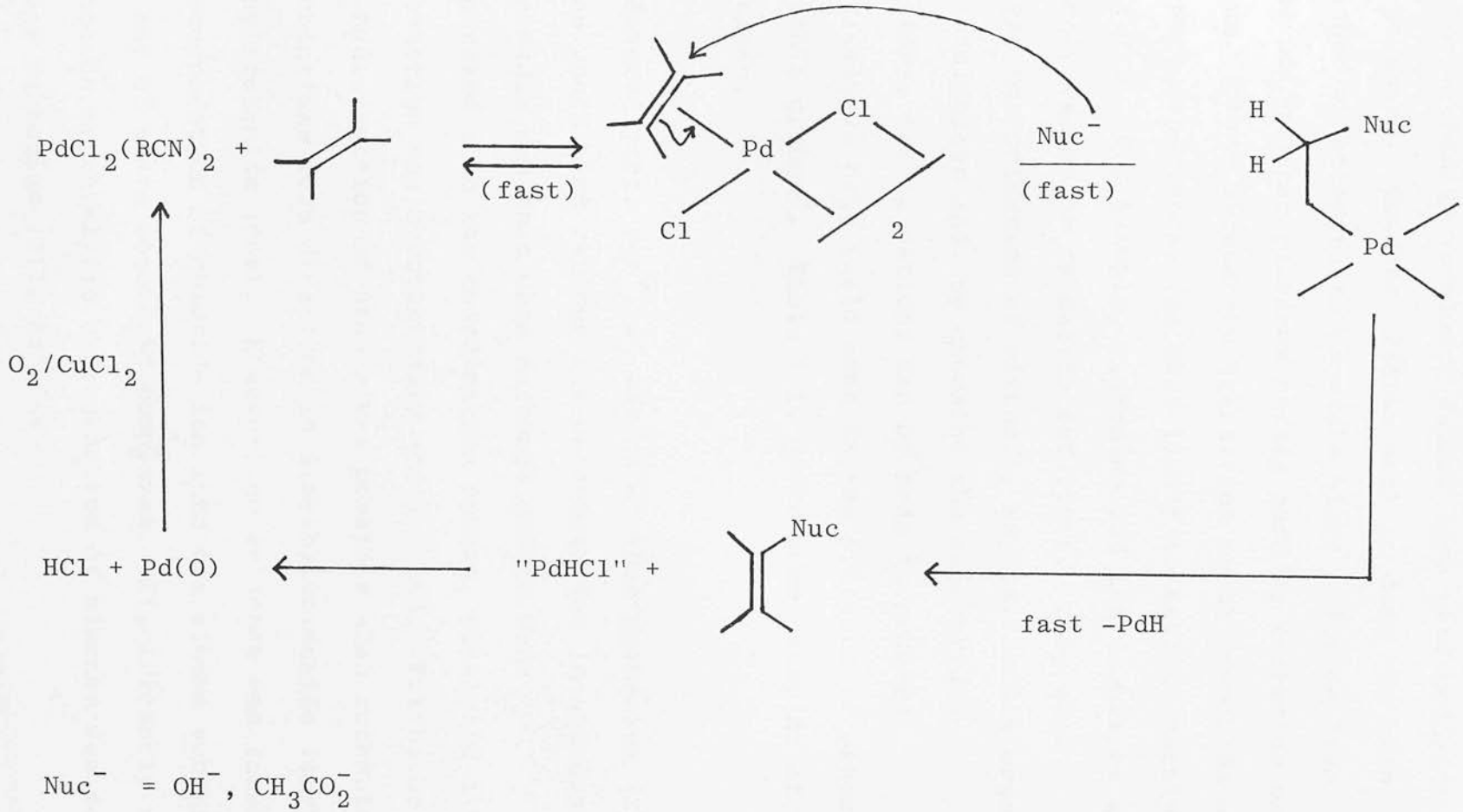
More recently a Cu(II)-catalysed oxychlorination process has been developed in which vinyl chloride is produced from ethene and hydrogen chloride (Equ.3).

$$CH_2 = CH_2 + HCl \xrightarrow[Cu]{[O]} CH_2 = CHCl + H_2O \quad \ldots \quad (3)$$

The oxychlorination process releases vinyl chloride production from the economics of the more costly raw material ethyne, whose manufacture is energy intensive. Ethyne obtained as a by-product of gas cracking is less expensive, but has not been available in sufficient volume to supply the large (10^9lbs p.a.) vinyl chloride production units.[1]

The oxidation of ethene to ethanal or vinyl acetate using palladium (II) and copper (II) salts as co-catalysts (the Wacker process) is well documented[2] (Scheme 1.1). Although after thirty years the mechanism of this process is still somewhat controversial, it is well established that the key step amounts to nucleophilic attack of water or acetate ion on the ethene bound to palladium. In general, the role of the copper (II) salts employed is to re-oxidise palladium (O) to palladium (II), and many of these processes have now been developed commercially.

SCHEME 1.1. THE WACKER PROCESS

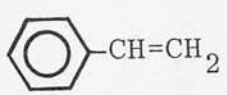
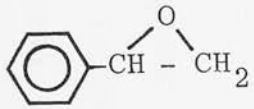
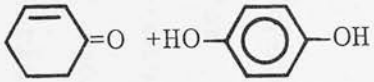
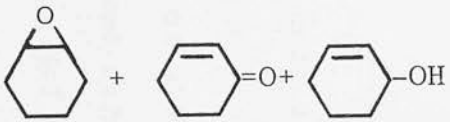
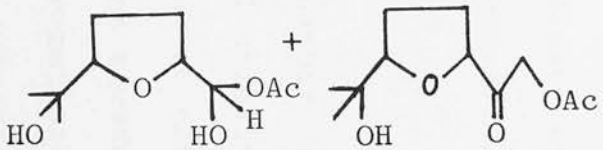


Nuc^- = OH^-, $CH_3CO_2^-$

It is established that vinyl chloride as well can be synthesised from ethene using palladium catalysts[3], and a reaction mechanism involving Wacker type intermediates has been proposed. However, little work to date has been published on attempts to generate vinyl chloride from ethene using other platinum metals such as ruthenium or rhodium. These second row transition metal compounds are, from past experience, the most likely to exhibit catalytic properties. For example, ruthenium and its complexes are extremely versatile oxidation catalysts. They will catalyse the oxidation of virtually any oxidisable organic functional group and, by choosing the appropriate conditions, the oxidations can be made to proceed selectively in high yield even in the presence of other oxidisable groups[4]. Table 1.1. gives some examples of such oxidations.

Several years ago[5], it was shown that ruthenium (II) halides would bind various alkene substrates in aqueous acidic media and that when carbonyl groups were incorporated into the coordination sphere, catalytic alkene hydrogenation was substantially accelerated. Furthermore, ready hydrogenation of ethene was possible when ruthenium (II) chlorides were dissolved in dimethylformamide (dmf) or dimethylacetamide (dma). However, no evidence was found for incorporation of chloride ion into the alkene substrate using any of these monomeric complexes. Significantly no interaction or catalytic hydrogenation of alkenes was found with any ruthenium (III) halides.

TABLE 1.1. Oxidation of Alkenes without Cleavage of the C=C bond[4]

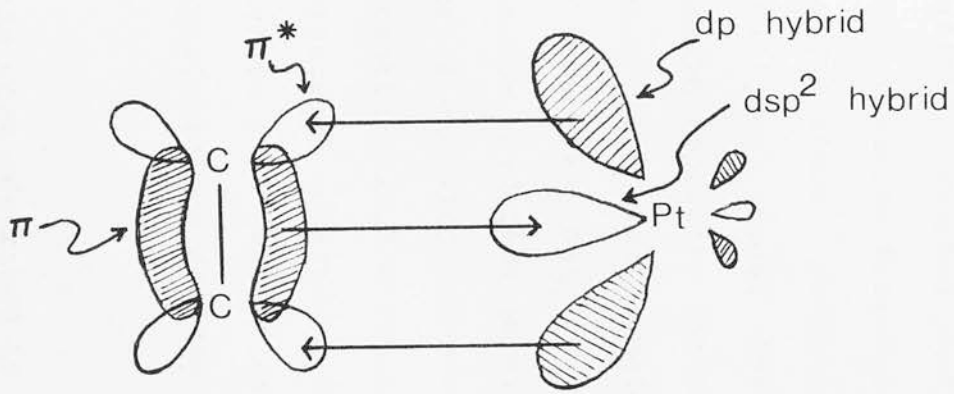
Substrate	Product	Catalyst	Oxidant	Yield per cent
$CH_3(CH_2)_6CH=CH_2$	$CH_3(CH_2)_6COOH + CH_3(CH_2)_6CH(O)CH_2$	$RuCl_2(PPh_3)_3$	O_2	30.5
		$RuCl_2(PPh_3)_3$	t-BuOOH	53
		$[Ru(trpy)(bipy)(H_2O)]^{2+}$	electricity	-
		$RuCl_2(PPh_3)_3$	O_2	27 (conv) ratio 1:5:3
		$RuCl_3$	$Na[IO_4]$	51,12

It is pertinent at this stage to consider the nature of the bonding of ethene to metals, as elucidated for Zeise's salt, $K[PtCl_3(C_2H_4)]$. This was prepared in 1827 and was the first example of a compound in which an organic moiety is bonded to a transition metal. In 1953 it was suggested that the bonding between ethene and platinum involved overlap of the occupied π orbital of ethene with an empty dsp^2 orbital of the d^8 Pt (II) as well as overlap of an occupied d (or dp hybrid) orbital of the Pt with the empty π^* orbital of ethene (Figure 1.1). The π^* orbital of ethene has the appropriate symmetry and energy to make this type of back-bonding of considerable importance in enhancing the stability of the alkene-Pt complex.[6] A similar situation is thought to exist in octahedral alkene-Ru(II) complexes whereas the Ru(III) valence state has insufficient electron density to back- donate to the π^* orbitals of alkenes and therefore no alkene-Ru(III) complexes have been isolated.

It is apparent from Scheme 1.1 that a number of factors may be important for catalysed vinyl chloride formation; namely (a) coordination of ethene to the metal centre; (b) activation of coordinated ethene towards nucleophilic attack by chloride ion; (c) promotion of nucleophilic attack on ethene rather than the metal ion, i.e. ethene modification rather than displacement, and (d) promotion of the β-hydride elimination step.

FIGURE 1.1.

Representation of the bonding between ethene and platinum in $K[PtCl_3(C_2H_4)]$



In recent years a number of triply- and doubly-halide-bridged binuclear complexes of ruthenium ranging from di-Ru(II) to di-Ru(III) systems e.g. $Ru_2(II,II)Cl_4L_{5-n}Y_n$ (n = 0,1,2)[7], $Ru_2(II,III)Cl_5L_{4-n}Y_n$ (n = 0,1)[7a,8] and $Ru_2(III,III)Cl_6L_3$ or $_4$[8] (L = various PR_3, AsR_3; Y = CO,CS) have been synthesised and fully characterised. Related studies reveal that a diversity of ligands (ranging from H_2O, NH_3[9] through P and As donors to π-bonded arene[10] moieties) can bind to the $(RuCl_2Ru)^{2+}$ and $(RuCl_3Ru)^{+}$ cores. The nature of these terminal ligands is an important factor in determining the redox behaviour of the binuclear complexes and voltammetric studies[8, 11] also establish that for many of these compounds, the various oxidation levels are accessible by successive reversible one-electron-steps localised on particular metal centres, with retention of gross structure. The electrode potentials associated with these steps are sensitive to such factors as the basicity of the bridging and terminal ligands and the isomeric form of the complex.

The aim of the work described in this thesis has been to synthesise analogous halide-bridged complexes containing alkene terminal ligands and to investigate their reactions with chloride ion and other nucleophiles. It was proposed that on binding to a ruthenium (II) centre the alkene substrate could be activated towards nucleophilic attack by the presence of an adjacent electron-withdrawing ruthenium (III) centre separated by halide bridges. By analogy with

earlier work[7, 8, 11] these Ru_2 (II, III) systems could be generated by either electrochemical or chemical methods, and their reactivity controlled by facile electronic switching (valence cycling). Recent work on η^6-arene ruthenium (II)[12] and η^5-pentamethylcyclopentadienyl-rhodium (III)[13] monomeric centres confirms that simple alkenes can indeed be readily activated towards nucleophilic attack. It appears in principle that the chloride-bridged systems offer several useful controllable features, for example: incipient coordinative unsaturation due to bridge opening or displacement of labile ligands; control of net charge and oxidation state at the binding site; ready electron, hydride, or chloride transfer involving the adjacent metal centre; and lastly, substantial modification of electrode potential, overall charge, steric environment, and solubility <u>via</u> strategic variation of the terminal groups.

After a brief general introduction to pertinent ruthenium chemistry, the remaining sections of this chapter discuss the wide variety of mostly monomeric alkene, alkyne and dinitrogen complexes of ruthenium (II). Dinitrogen complexes are included since their methods of preparation are very often closely related and because new examples figure importantly in this thesis. The final sections provide a more detailed account of the characteristic properties of triply-halide-bridged binuclear ruthenium complexes with which this work is intimately concerned.

1.2. GENERAL INTRODUCTION TO RUTHENIUM CHEMISTRY

Ruthenium (atomic number 44, electronic configuration $[Kr]4d^7 5s^1$, atomic weight 101.07) exhibits a wide range of oxidation states from (VIII) to (-II). The most common of these are (III) and (II), associated largely with ligands which are good σ-donors but which show no substantial π-acceptor or donor properties, i.e. the "classical" ligands H_2O, NH_3 *etc*. The least common oxidation states are (VII), (V), (I) and (-I), Small π-donor ligands such as F^-, O^{2-}, N^{3-} stabilise the higher oxidation states (e.g. $Ru(VI)F_6$, $Ru(VIII)O_4$, $[Ru(VI)NCl_4]^-$) whereas the lower oxidation states are stabilised by π-acceptor ligand sets comprised of CO, PR_3 *etc*. (e.g. $[Ru(-II)(CO)_4]^{2-}$, $Ru(O)(CO)_5$, $Ru(O)(CO)_3(PPh_3)_2$).

The complexes described in this work are all of Ru(II) or Ru(III) so there follows a brief account of areas of interest involving complexes of these ions.

Almost all Ru(II) (d^6) complexes are octahedral and diamagnetic with a t_{2g}^6 configuration (in the absence of steric constraints). Such complexes can be prepared with carbonyl, phosphine, arsine, ammine and heterocyclic ligands, so that the range is very wide. Major advances in recent years have been in areas as diverse as homogeneous catalysis using Ru(II) tertiary phosphine complexes, kinetic studies on substitution reactions of $[Ru(NH_3)_5L]^{2+}$

and the photophysics and photochemistry of $[Ru(bipy)_3]^{2+}$ and related systems.

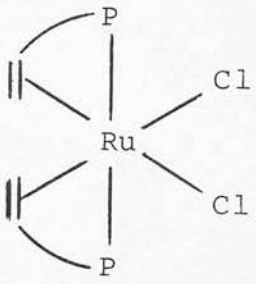
Ru(III) (d^5) complexes are octahedral low spin t_{2g}^5 species with one unpaired electron and are usually inert to substitution. "Classical" ligands (e.g. NH_3, H_2O, halides) are often associated with Ru(III) and current areas of active interest include the electronic structure of polynuclear carboxylates and complexes of the type $[\{Ru(NH_3)_5\}_2L]^{5+}$ which are mixed-valence Ru_2(II/III) species. The degree of unpaired electron delocalisation (or metal-metal interaction) is the main feature of interest in these compounds.

1.3. ALKENE, ALKYNE AND DINITROGEN COMPLEXES OF RUTHENIUM(II)

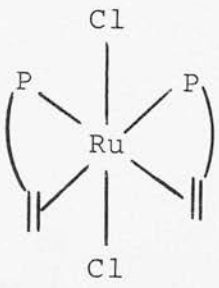
1.3.1. Alkene Complexes

Although stable complexes of ruthenium(II) with chelating di-alkenes such as 1,5- cyclooctadiene, norbornadiene, cyclooctatetraene and cycloheptatriene are well known, it was not until 1974 that the analogous mono-alkene complexes were described[16]. These were prepared by reaction of "$RuCl_3xH_2O$" with (2-vinylphenyl) diphenylphosphine, (O-styryl-diphenyl-phosphine, SP), in boiling ethanol or 2-methoxyethanol giving a complex of formula $RuCl_2(SP)_2$. In 2-methoxyethanol a deep yellow

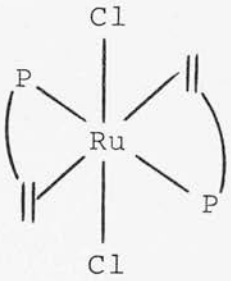
isomer (1) was obtained, but in ethanol an inseparable mixture of two other yellow isomers (2) and (3) was formed, which slowly isomerised to (1) on heating in 2-methoxyethanol.



(1)



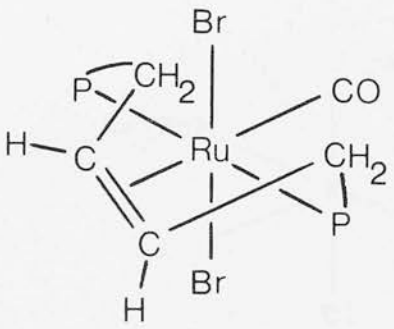
(2)



(3)

Spectroscopic data (^{1}H, ^{31}P n.m.r., i.r.) confirmed that both vinyl groups were coordinated in all three isomers. Ru(II) complexes containing one bidentate SP ligand resulted from the reaction (in 2-methoxyethanol in an atmosphere of CO) of "$RuCl_3.xH_2O$" with <2 moles of SP per gram-atom of ruthenium. The white crystalline complex $RuCl_2(CO)_2SP$ contains bidentate SP, cis-carbonyl ligands and cis-chlorine atoms. On heating this complex in 2-methoxyethanol in the absence of CO a dimeric monocarbonyl compound $[RuCl_2(CO)SP]_2$ was obtained as a mixture of isomers. The zerovalent ruthenium complex containing a substituted butadiene ligand which results from the extended reaction of $Ru_3(CO)_{12}$ and excess SP in boiling n-nonane undergoes addition of two molecules of HCl or HBr to give crystalline monomeric Ru(II) complexes containing the tridentate alkene ligand bis-1,4-[o-(diphenylphosphino)phenyl]-cis-2-butene, i.e.

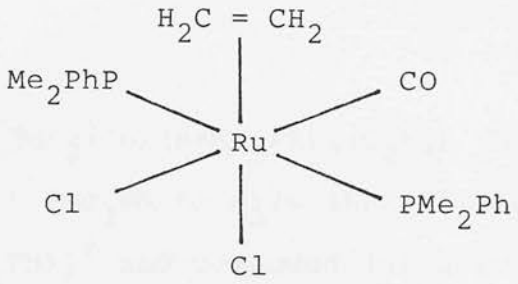
$RuX_2(CO)o\text{-}Ph_2PC_6H_4CH_2CH{=}CHCH_2C_6H_4PPh_2\text{-}o$ ($X = Cl^-, Br^-$). Both compounds exist in isomeric forms, but the more stable form ($X = Br^-$) has been shown by X-ray crystallography to have configuration (4) with <u>trans</u>-bromine atoms and a CO group <u>trans</u> to the alkene.[17]



(4)

Treatment of a solution of $[Ru(NH_3)_5(H_2O)]^{2+}$ (freshly prepared from $[RuCl(NH_3)_5]Cl_2$, $Ag[O_2CF_3]$ and zinc amalgam) with the appropriate alkene gives the complexes $[Ru(NH_3)_5(alkene)]^{2+}$ (alkene = ethene, isobutene, cyclohexa-1,4-diene, fumaric acid). The complexes may be isolated as the $S_2O_6^{2-}$ or PF_6 salts. Evidence for Ru(4d) -> π^* back-bonding is provided by the shift to lower frequencies of $\nu_{C=C}$ in their i.r. spectra and the shift towards the corresponding alkane region (to lower frequency) in their 'H n.m.r. spectra.[18]

An X-ray crystallographic study of $RuCl_2(CO)(PMe_2Ph)_2(C_2H_4)$ (5), prepared by treating all-trans-$RuCl_2(CO)_2(PMe_2Ph)_2$ with ethene in chloroform[19], shows that the C = C bond is essentially parallel to the Ru-P bonds. This allows overlap of the ethene π^* orbitals with a Ru d-orbital which is not suitably positioned to interact with CO, the other good π-electron acceptor in the molecule.

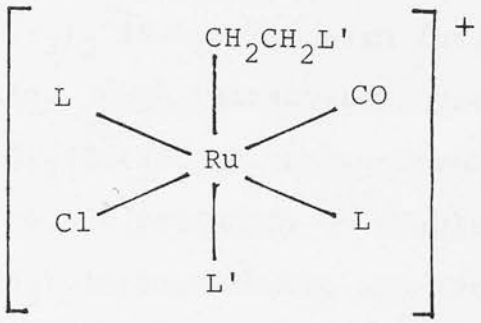


(5)

Retention of this structure in solution is indicated by ^1H and ^{13}C n.m.r. studies, although a single proton resonance for all four ethene protons is observed down to -233K, consistent with rotation of the ethene group about the Ru-ethene axis.[19]

Of direct relevance to the work presented in this thesis is the reaction of (5) with the nucleophile PMe_2Ph. Although at 308K this results simply in substitution of the ethene ligand, low temperature studies reveal that the kinetically favoured product is the cation

$[RuCl(CO)(PMe_2Ph)_3(CH_2CH_2PMe_2Ph)]^+$ (6)



L = L' = PMe_2Ph

(6)

The complexes $RuX_2(CO)(AsMe_2Ph)_2(C_2H_4)$ ($X = Cl^-, Br^-$) react similarly with PMe_2Ph to give $(RuX(CO)(AsMe_2Ph)_2(PMe_2Ph)(CH_2CH_2PMe_2Ph)]^+$ and compound (5) also reacts with $PMePh_2$ to form $[RuCl(CO)(PMe_2Ph)_2(PMePh_2)(CH_2CH_2PMePh_2)]^+$. The first step in these reactions is probably nucleophilic attack on the coordinated ethene ligand followed by displacement of the halide ion <u>trans</u> to the newly formed alkyl ligand. [21]

Treatment of $RuCl(CO)_3(\eta\text{-}C_3H_5)$ with acrylonitrile (CH_2=CHCN,acn) in toluene results in evolution of CO and formation of the dimeric complex $[RuCl(CO)_2(\eta'\text{-}C_3H_5)(\eta^2\text{-acn})]_2$ which contains a η^2-coordinated acrylonitrile and a σ-bonded allyl ligand. Triphenylphosphine cleaves the halogen bridge in this complex to give $RuCl(CO)_2(\eta'\text{-}C_3H_5)(PPh_3)(\eta^2\text{-acn})$ [22].

The pale yellow complexes $RuCl_2(CO)(PCy_3)_2$(alkene) are precipitated from benzene when the five-coordinate $RuCl_2(CO)(PCy_3)_2$ is treated with fumaronitrile or acrylonitrile. With tetracyanoethylene a blue dinuclear complex $[RuCl_2(CO)(PCy_3)]_2$tcne, presumably containing bridging tcne, is produced. [23] Stable 1:1 adducts, $RuCl(NO)(PPh_3)_2$(cyanoalkene), are formed on reaction of $RuCl(NO)(PPh_3)_2$ with tcne or fumaronitrile in benzene. These brown solids are proposed to have a configuration with <u>cis</u>-phosphine ligands and Cl <u>trans</u> to NO. [24]

Reactions of $Ru(\eta\text{-}C_5H_5)(PMe_3)_2Cl$ with various alkenes and alkynes, followed by NH_4PF_6 addition, lead to Cl^- loss and isolation of the complexes $[Ru(\eta\text{-}C_5H_5)(PMe_3)_2$(alkene)$]PF_6$ (alkene = C_2H_4, CH_2=CHMe, CH_2=CHPh, CH_2=CHCN, (E)-CHCl=CHCl, (Z)-EtO_2CCH=CHCO_2Et, ½ COD). [25, 26] Attempts to prepare analogous PPh_3 derivatives such as $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2L]^+$(L = C_2H_4, C_2Ph_2, HC_2PH) were unsuccessful. [27] The marked contrast in reactivity of the PMe_3 and PPh_3-containing starting materials was attributed to the relative sizes of the tertiary phosphines (cone angles: PMe_3, 118°; PPh_3, 145°).

1.3.2. <u>Alkyne complexes</u>

Ruthenium(II) cations containing π-bonded alkynes, $[(Ru(NH_3)_5(alkyne)]^{2+}$ (alkyne = ethyne, phenylacetylene, 3-hexyne) can be prepared in an analogous fashion to the previously discussed alkene complexes (Section 1.3.1.).

The shift to lower wavenumber ($\Delta\nu$ 120-220 cm^{-1}) of the $\nu_{C\equiv C}$ stretching frequency on coordination is good evidence for strong back-bonding from metal to alkyne. The ^{1}H n.m.r. spectra of the complexes exhibit a shift to higher frequency of the terminal alkyne proton signals of about 1-2 p.p.m., and thus approach the region expected for the corresponding alkenes. Formal reduction potentials obtained by cyclic voltammetric studies reveal the stabilisation of Ru(II) relative to Ru(III) resulting from the strong back-bonding to the alkyne ligand. [18]

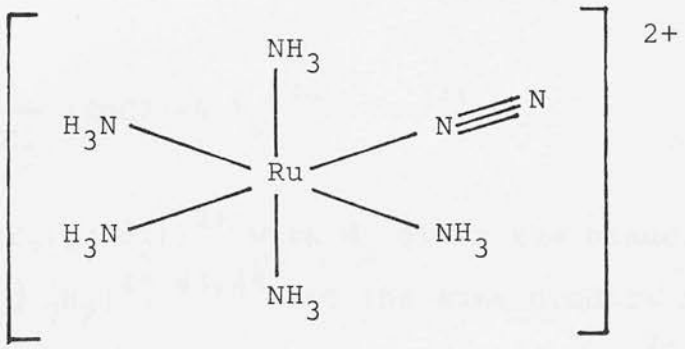
The alkyne complexes $[Ru(\eta\text{-}C_5H_5)(PMe_3)_2(alkyne)]PF_6$ (alkyne = $EtC\equiv CEt$, $PhC\equiv CPh$, $(MeO_2C)\equiv C(CO_2Me)$) are prepared in the same way as their alkene analogues [25] (see Section 1.3.1.).

Reactions of all trans-$RuCl_2(CO)_2(EMe_2Ph)_2$ (E = P,As) with the alkynes $(RO_2C)C\equiv C(CO_2R)$ (R = Me,Et) give the alkenyl complexes $RuCl(CO)_2(EMe_2Ph)_2[C(CO_2R)=C(CO_2R)Cl]$. The proposed mechanism of formation involves initial formation of the alkyne complexes $RuCl_2(CO)(EMe_2Ph)_2[(RO_2C)C\equiv C(CO_2R)]$ which then undergo intramolecular nucleophilic attack involving chloride ligand transfer. Further reaction (R = Me) with EMe_2Ph gives $RuCl(CO)(EMe_2Ph)_3[C(CO_2Me)=C(CO_2Me)Cl]$. [28]

1.3.3. Dinitrogen complexes

The synthesis of $[Ru(NH_3)_5N_2]^{2+}$ was first reported in

1965 and involved refluxing "$RuCl_3xH_2O$" in aqueous hydrazine. [29] This was the first complex of a transition metal recognised to contain N_2 as a neutral ligand. A remarkable feature of the chemistry of the dinitrogen complexes of the ruthenium-pentaammine series is the large number of quite different routes available for their preparation. [30-33] The linear linkage of N_2 in $[Ru(NH_3)_5N_2]^{2+}$ (7) has been confirmed by X-ray analysis. [34]



Ru-N = 2.11Å

N≡N = 1.12Å

(7)

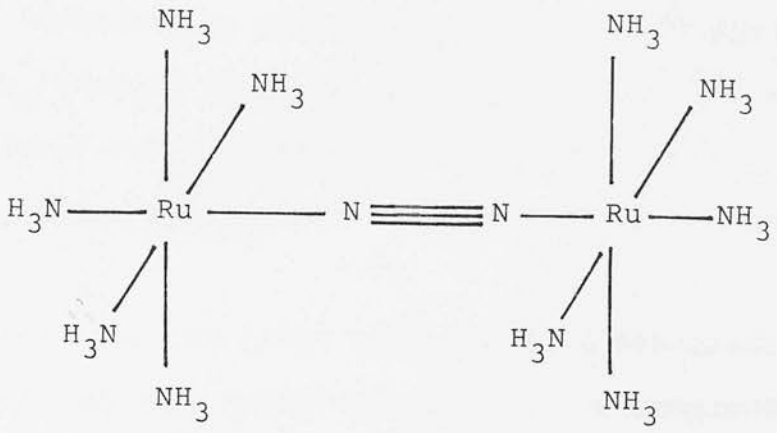
Counterion and solvent have a marked effect on the frequency (2100-2170 cm^{-1}) and intensity of the $\nu_{N\equiv N}$ stretching mode in the i.r. spectra and this has been attributed to electrostatic interactions in solution. [35,36,37] On oxidation ($E_{½}$ = +0.72V vs S.C.E.) this complex decomposes with loss of the N_2 ligand. Also, reaction of $[Ru(NH_3)_5N_2]^{2+}$ with $\dot{O}H$ radicals yields $[Ru(III)(NH_3)_5N_2]^{3+}$ which rapidly aquates to form $[Ru(III)(OH)(NH_3)_5]^{2+}$. [39] These observations provide further confirmation of the role that metal to N_2

back-bonding plays in stabilising the complex and of the inability of Ru(III) to effectively bind N_2.

In common with many other dinitrogen complexes the N_2 ligand in $[Ru(NH_3)_5N_2]^{2+}$ may be displaced by other ligands; thus, with pyridine $[Ru(NH_3)_5py]^{2+}$ and $[Ru(NH_3)_4py_2]^{2+}$ are formed.[40] Ligand substitution under photolytic conditions occurs via ligand field excited states and involves oxidation of Ru(II) to Ru(III) [41,42,43] (Equ. 4)

$$[Ru(NH_3)_5N_2]^{2+} \xrightarrow[HCl]{h\nu} [RuCl(NH_3)_5]^{2+} \quad \ldots (4)$$

Treatment of $[Ru(NH_3)_5(OH_2)]^{2+}$ with N_2 gives the binuclear cation $[\{Ru(NH_3)_5\}_2N_2]^{4+}$ [43,44] and the same product is formed by intermolecular coupling of $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[Ru(NH_3)_5N_2]^{2+}$. [43,45] Other routes to this binuclear complex include zinc amalgam reduction of reaction solutions of N_2O and $[RuCl(NH_3)_5]^{2+}$, [46] reaction of $[Ru(NO)(NH_3)_5]^{3+}$ with $[Ru(NH_3)_6]^{3+}$ under basic conditions [47] and decomposition of $[Ru(NH_3)_5(N_3)]^{2+}$ under acidic conditions.[48] Single crystal X-ray studies reveal that the complex has the linear structure (8).[49]



(8)

The N-N distance (1.124 Å) is consistent with back-donation of electron density from Ru(II) to N_2[50] (N-N = 1.098Å for free N_2).

The mixed valence $[II,III]^{5+}$ ion can be generated by oxidation of the $[II,II]^{4+}$ complex, (which shows two, one-electron oxidations at +0.73V and +1.2V vs S.C.E.),[38,51] with Br_2 or Ce^{4+}.[51,52] Oxidation of $[Ru(NH_3)_5]_2N_2^{5+}$ at 1.2V gives the $(III,III)^{6+}$ cation.[51]

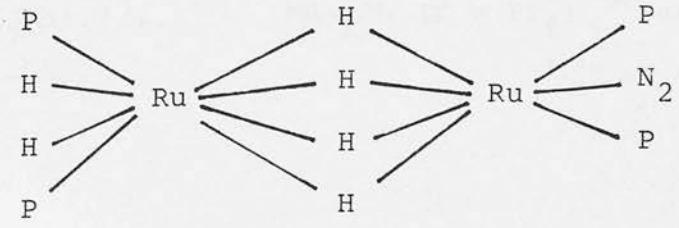
The complex $[\{Ru(H_2O)_5\}_2N_2][BF_4]_4$ is obtained on treatment of $[Ru(H_2O)_6]^{2+}$ (generated in 0.1M trifluoromethylsulphonic acid solution by reduction of $[RuCl_5(H_2O)]^{3+}$ with H_2) with N_2 at 5 atmospheres in 1M HBF_4. A weak i.r. band at 2080 cm^{-1} has been assigned to $\nu_{N\equiv N}$.[53]

Several dinitrogen complexes of Ru(II) containing tertiary phosphine ligands have been prepared. Thus,

reaction of $RuHCl(PPh_3)_3$ with $AlEt_3$ and N_2 in diethyl ether gives $RuH_2(N_2)(PPh_3)_3$ with $\nu_{N\equiv N}$ at 2147 cm^{-1} [54], whereas the more soluble $RuH_2(N_2)(Ptol_3)_3$ is synthesised by reaction of $RuCl_2(Ptol_3)_3$ with $NaBH_4$ and N_2 in ethanol. [54]

In contrast to the range of N_2-bridged binuclear species, there are few examples of binuclear complexes containing terminally bound N_2. The compound $(Ph_3P)_2ClRuCl_3Ru(N_2)(PPh_3)_2$ is formed by treating a thf solution of $RuCl_2(PPh_3)_4$ in a reverse osmosis cell with nitrogen under pressure.[55] Attempts to prepare this complex in this department and in the laboratories of the New Science Group of Imperial Chemical Industries plc have been unsuccessful due to difficulties encountered in reproducing the required reaction conditions.

The novel compound $Ru_2H_6(N_2)(PPh_3)_4$ can be prepared by recrystallisation under nitrogen of the hydrogenation product of $Ru(PPh_3)_2(styrene)_2$. A preliminary X-ray analysis indicated structure (9) with four bridging hydride ligands and a short Ru-Ru distance (2-556(3)Å) consistent with a Ru-Ru double bond.[56]



(9)

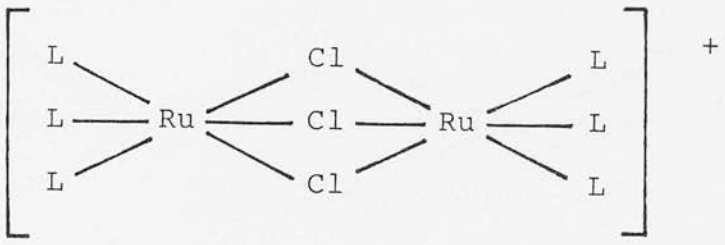
However, very recent studies suggest that this compound should be reformulated as the triple-hydride-bridged $Ru_2H_4(N_2)(PPh_3)_4$,[57] analogous to $Ru_2Cl_4(N_2)(PPh_3)_4$ described above.

1.4. TRIPLY-HALIDE-BRIDGED BINUCLEAR RUTHENIUM COMPLEXES

1.4.1. Di-Ruthenium (II) Complexes

In 1961 reactions of "$RuCl_3xH_2O$" with L (L = various alkyl and aryl substituted PR_3) in aqueous MeOH or EtOH were reported by Chatt to give binuclear complexes of type $[L_3RuCl_3RuL_3]Y$ (Y = Cl^-,ClO_4^-,SCN^-,BPh^-_4).[58] Since then a variety of synthetic routes to these cations has been developed e.g. reaction of $[RuCl_2(nbd)]_n$, $RuCl_2(PPh_3)_x$ (x = 3 or 4) or the reduced "ruthenium blue" solution with L in polar media. The range of such cations has also been extended to include L = $P(OR)Ph_2$, $P(OR)_2Ph$, $P(OR)_3$ (R = Me,Et), $AsRPh_2$, AsR_2Ph etc.[46,59-67]

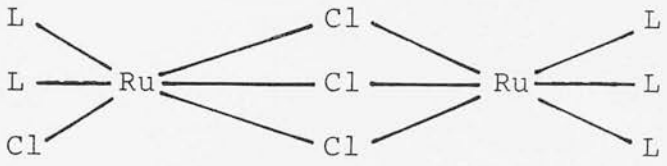
X-ray structural analyses have confirmed the confacial bioctahedral geometry (10) for L = PEt_2Ph (Y = <u>mer</u>-$[RuCl_3(PEt_2Ph)_3]^-$),[68] PMe_2Ph (Y = PF^-_6)[69] and PMe_3 (Y = BF^-_4).[70]



(10)

Treatment of the cation $[RuH(NH_2NMe_2)_3(cod)]^+$ with an excess of L in acetone/MeOH followed by addition of HX affords the related cations $[L_3RuX_3RuL_3]^+$ ($X = OH^-$, $L = PMe_2Ph$, $PMePh_2$, $P(OMe)Ph_2$; $X = F^-$, I^-, SH^-, SR^-, $L = PMe_2Ph, PMePh_2$). [71] Reaction of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ and $[Ph_3C]BF_4$ in thf gives the hydroxo-bridged cation, [72] for which a crystal structure has been published. When treated with HX in $MeNO_2$, these hydroxo-complexes give high yields of the pure $[Ru_2X_3L_6]^+$ cations ($L = PMe_2Ph$; $X = Cl^-$, Br^-, I^-). [73] Earlier alternative routes to the iodo- and bromo-species involved treatment of $[Ru_2Cl_3L_6]^+$ with NaI and reaction of "$RuCl_3xH_2O$" with LiBr and L, [67] but recent ^{31}P n.m.r. data indicate that these methods lead to mixtures of $[Ru_2Cl_nX_{3-n}L_6]^+$ cations. [73]

The neutral binuclear complex $Ru_2Cl_4(PEt_2Ph)_5$ (and/or ionic $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$) results from pyrolysis of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in methylacetate or n-propyl-propionate and the structure (11) has been confirmed by X-ray analysis. [68,74,75]



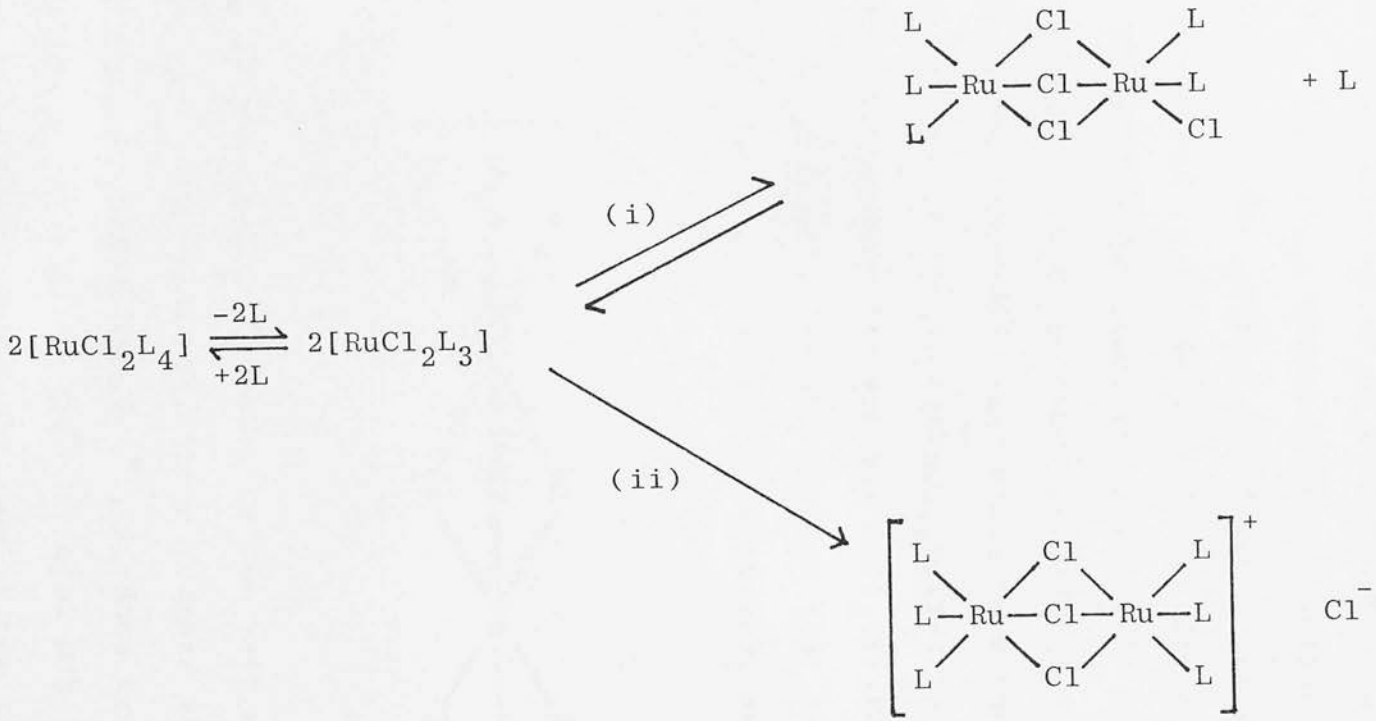
$L = PEt_2Ph$

(11)

Scheme 1.2 summarises an alternative route (developed in this laboratory) to the neutral species (11) which involves exchange reactions of $RuCl_2(PPh_3)_3$ with L ($L = PClPh_2$, $PEtPh_2$, PEt_2Ph) in non-polar solvents such as hexane or petroleum ether. In polar solvents the ionic complexes $[Ru_2Cl_3L_6]Cl$ are formed. The mechanism in both types of solvent is proposed to involve intermolecular coupling of monomeric $RuCl_2L_{3 \text{ or } 4}$ species.[46] The neutral $Ru_2Cl_4L_5$ species are not produced by any of these routes when $L = P(OR)_2Ph$ or $P(OR)Ph_2$, and this is attributed to the increased inertness of the Ru-P bonds. The species isolated from these reactions are $[Ru_2Cl_3L_6]^+$, $[RuCl(P(OMe)Ph_2)_4]^+$, $[RuCl(P(OEt)Ph_2)_4]_2^{2+}$ and $[Ru_3Cl_5(P(OEt)Ph_2)_9]^+$.[63]

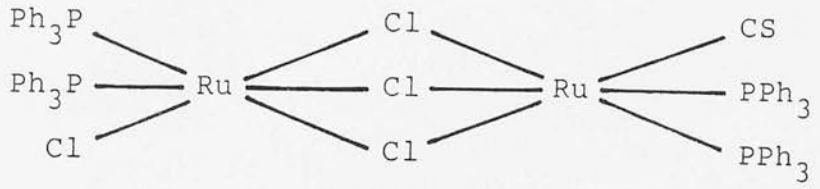
Treatment of $RuCl_2(PPh_3)_3$ with CS_2 gives the neutral binuclear complex $Ru_2Cl_4(CS)(PPh_3)_4$ (12), the structure of which has been confirmed by X-ray analysis.[76] Some double-chloride-bridged $[RuCl_2(CS)(PPh_3)_2]_2$ and $RuCl_2(S_2CPPh_3)(PPh_3)_2$ are also obtained.[4a,77]

Scheme 1.2 Coupling reactions of $RuCl_2L_{3 \text{ or } 4}$ complexes



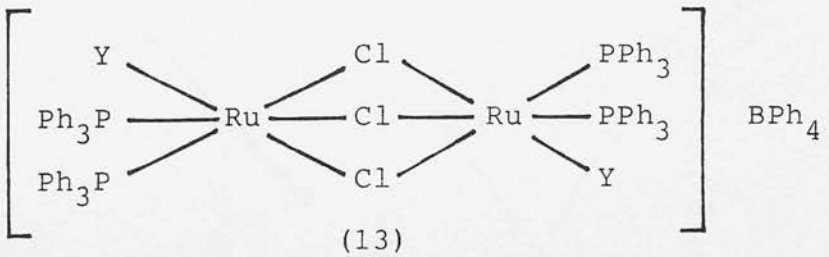
(i) Non-polar solvent

(ii) Polar solvent



(12)

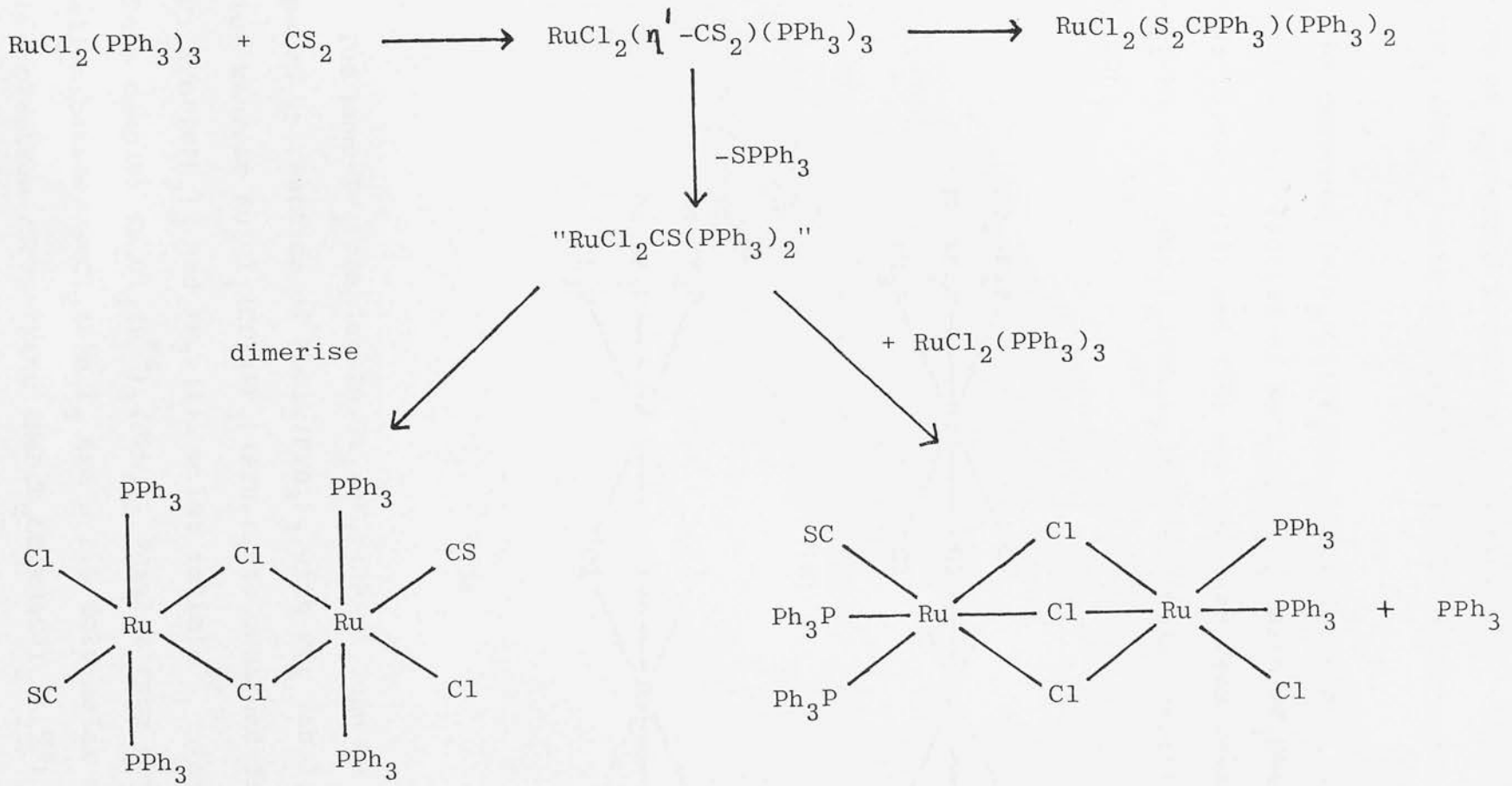
The high yields of $Ru_2Cl_4Y(PR_3)_4$ (Y = CO, CS; PR_3 = PPh_3, P(p-tol)$_3$) obtained from reaction of $RuCl_2(PPh_3)_3$ and $RuCl_2Y(PR_3)_2$dmf support the reaction pathway presented in Scheme 1.3.[4a,d] The mixed phosphine complex $(Ph_3P)_2(CO)RuCl_3RuCl(P(p\text{-}tol)_3)_2$[4d] and the heterobimetallic $(Ph_3P)_2(CO)RuCl_3OsCl(PPh_3)_2$[78] may also be prepared by this intermolecular coupling method. An isomeric mixture of $(Ph_3P)Cl(Y)RuCl_3Ru(Y)(PPh_3)_2$ complexes is obtained on heating the monomer $RuCl_2(Y)(PPh_3)_2$MeOH (Y = CO, CS) in CH_2Cl_2 and the cations (13) are then prepared by treating this mixture with PPh_3 and $NaBPh_4$.[4a]



(13)

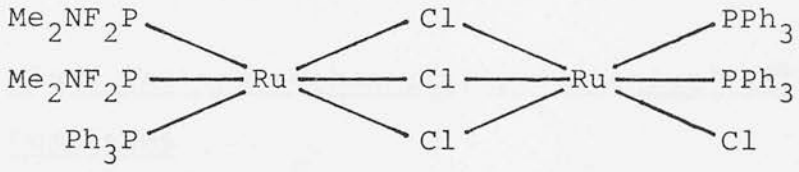
Reaction of the $[RuCl_3(CO)(nbd)]^-$ anion with an excess of PPh_3 in CH_2Cl_2 also gives the three isomers of $(Ph_3P)Cl(CO)RuCl_3Ru(CO)(PPh_3)_2$[4a], as does treatment of $RuHX(CO)(PPh_3)_3$ (X = H^-[79], Cl^-[80]) with HCl in benzene or elimination of $SnCl_2$ from $Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3$.[81]

SCHEME 1.3. Reaction of $RuCl_2(PPh_3)_3$ with CS_2

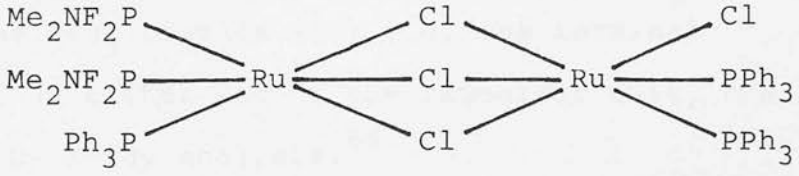


The analogous $Ru_2Cl_4(PF_3)_2(PPh_3)_3$ can be prepared as a mixture of geometric isomers by reaction of $RuH_2(PF_3)(PPh_3)_3$ with HCl and by various other methods. [79]

The compound $(PPh_3)Cl(PF_2NMe_2)RuCl_3Ru(PF_2NMe_2)(PPh_3)_2$ is obtained on reaction of $RuCl_2(PPh_3)_3$ with PF_2NMe_2 whereas isomers (14) and (15) are obtained from reaction of all-<u>cis</u>-$RuCl_2(PF_2NMe_2)_2(PPh_3)_2$ with equimolar amounts of $RuCl_2(PPh_3)_3$. [79]



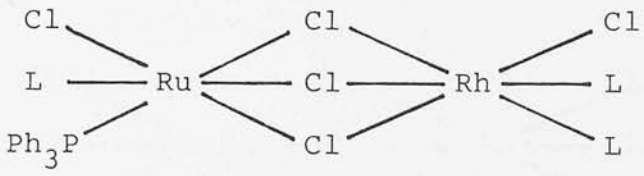
(14)



(15)

The mono-PF_3 complex $Ru_2Cl_4(PF_3)(PPh_3)_4$ can be prepared by reaction of $RuCl_2(PPh_3)_3$ with PF_3 (in 2:1 molar ratio) whereas $Ru_2Cl_4(CO)(PF_3)(PPh_3)_3$ is obtained from $Ru_2Cl_4(CO)(PPh_3)_4$ and PF_3 (1:1 molar ratio). [79] The carbene complex $Ru_2Cl_4(L^{Me})_3(PPh_3)_2$ results from the reaction between $RuCl_2(PPh_3)_3$ and a 1.5 fold molar excess of the electron rich alkene $(MeNCH_2CH_2NMeC=)_2(L_2^{Me})$. [82]

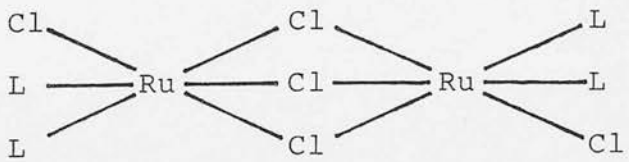
Finally, the heterobimetallic complexes (16) are synthesised by intermolecular coupling of equimolar amounts of $RuCl_2(PPh_3)_3$ and mer-$RhCl_3L_3$ (L = PMe_2Ph, PEt_2Ph, PBu_3, PBu_2Ph, PPh_3).[83]



(16)

1.4.2. Mixed Valence Ruthenium(II)/Ruthenium(III) Complexes

The prolonged reaction of an excess of L and "$RuCl_3xH_2O$" in EtOH was reported in 1967 to give the complexes $Ru_2Cl_5L_4$ (L = PBu_3, $Ppent_3$).[84] The "symmetric" structure of the PBu_3 complex (17) i.e. one terminal chloride ligand at either end of the binuclear unit, has been confirmed by X-ray analysis.[85]

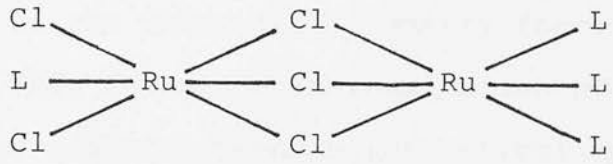


L = PBu_3

(17)

These were the first formally mixed-valence Ru_2(II,III) complexes containing a triple-chloride-bridge. Reaction

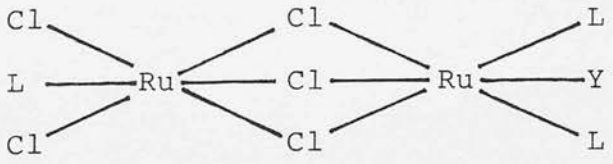
of "$RuCl_3xH_2O$" with an excess of AsR_3 in EtOH ($As(p\text{-}tol)_3$) or butan-2-ol ($AsPh_3$) have since given the tertiary arsine analogues of (17).[5b] The isomer (18) is obtained from reaction of "$RuCl_3xH_2O$" with $As(p\text{-}tol)_3$ in butan-2-ol or $As(pPhCl)_3$ in MeOH.



L = $As(p\text{-}tol)_3$, $As(pPhCl)_3$, PEt_2Ph

(18)

Deliberate aerial oxidation of $Ru_2Cl_4(PEt_2Ph)_5$ (11) in $HCl/MeNO_2$ gives $Ru_2Cl_5(PEt_2Ph)_4$ (18), the "asymmetric" structure being confirmed by X-ray analysis.[5b] Structure (19) has been assigned to the products of aerial oxidation of $(PR_3)_2YRuCl_3RuCl(PR_3)_2$ (Y = CO,CS; R = Ph, p-tol).[4a,5a,73,78]



(19)

The related mixed valence complexes $Ru_2Cl_5(mppl)_4$ (mppl = 3-methyl-1-phenylphosphole)[86] and $Ru_2Cl_5(dpae)_2$[5b] are also known.

The mixed valence species $[Ru_2Cl_3(PEt_2Ph)_6]^{2+}$, $[Ru_2Cl_4(PEt_2Ph)_5]^{+}$, $[Ru_2Cl_4Y(PPh_3)_4]^{+}$ (Y = CO,CS), $[Ru_2Cl_6(As(p\text{-}tol)_3)_3]^{-}$ and others have been characterised by <u>in situ</u> spectroscopic techniques after electrochemical generation from stable Ru_2(II,II) or Ru_2(III,III) complexes. The degree of metal-metal interaction has been found to decrease as the molecular asymmetry increases in these complexes. This follows from examination of the intervalence charge transfer band in the optical spectra. Equally, Ru_2(II,II) anions such as $[(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3]^{-}$ and $[(As(p\text{-}tol)_3)Cl_2RuCl_3RuCl(As(p\text{-}tol)_3)_2]^{2-}$ have been electrogenerated in bulk from Ru_2(II,III) or Ru_2(III,III) precursors and characterised <u>in situ</u>.[73,87]

These closing observations are directly relevant to our hopes of assembling variable-valence alkene-di-ruthenium complexes.

CHAPTER 2

TERMINAL HALIDE SUBSTITUTION IN NEUTRAL TRIPLE-HALIDE-BRIDGED BINUCLEAR RUTHENIUM (II) COMPLEXES

CHAPTER 2. TERMINAL HALIDE SUBSTITUTION IN NEUTRAL TRIPLE-HALIDE-BRIDGED BINUCLEAR RUTHENIUM (II) COMPLEXES.

2.1. INTRODUCTION

The incorporation of neutral ligands into metal complexes by displacement of terminal halide ligands is a widely observed phenomenon. The loss of the halide ligand is often assisted by use of a halide-abstracting agent and in many cases the reaction does not proceed at all unless such a reagent is present. These reagents are very often simple metal salts such as $AgBF_4$, $NaBF_4$ and $TlBF_4$, the cations of which form halide salts which are poorly soluble in particular solvents. Ammonium salts are also frequently used.

The formation of the cationic complexes $[Ru(L)(\eta\text{-}C_5H_5)(PMe_3)_2]^+$ (L = various alkenes and alkynes)[25,26] by treatment of $RuCl(\eta\text{-}C_5H_5)(PMe_3)_2$ with NH_4PF_6 and L in methanol typify the type of reaction under consideration here. Various binuclear species have been prepared in this way, such as $[(Ph_3P)_2(CO)RuCl_3Ru(CO)(PPh_3)_2]^+$, which is obtained on treatment of $(Ph_3P)(CO)ClRuCl_3Ru(CO)(PPh_3)_2$ with $NaBPh_4$ and PPh_3 in CH_2Cl_2[4a]. The binuclear rhodium (III) cation $[(Et_2PhP)_2ClRhCl_3RhCl(PEt_2Ph)_2]^+$ has been prepared similarly by treatment of $(Et_2PhP)Cl_2RhCl_3RhCl(PEt_2Ph)_2$ with $AgBF_4$ and PEt_2Ph in ethanol.[88]

The work described in this chapter is concerned with abstraction of terminal halide (particularly chloride) from complexes of the type $(R_3P)_2XRuX_3Ru(PR_3)_2Y$ ($X = Cl^-, Br^-$; $Y = CO, CS, PR_3$) and incorporation of various ligands L = alkene, alkyne, dinitrogen, dmso, acetonitrile, nitromethane. The chloride-bridged species prepared in this way with L = ethene are the most important in the context of the ultimate aim of the work presented in this thesis, i.e. the catalytic conversion of ethene to vinyl chloride.

2.1.1. Electrochemical techniques

Since electrochemical studies have been carried out on some of the new species described in this and subsequent chapters, it is considered worthwhile at this point to give a brief outline of the techniques employed and the theory behind them.[88,90]

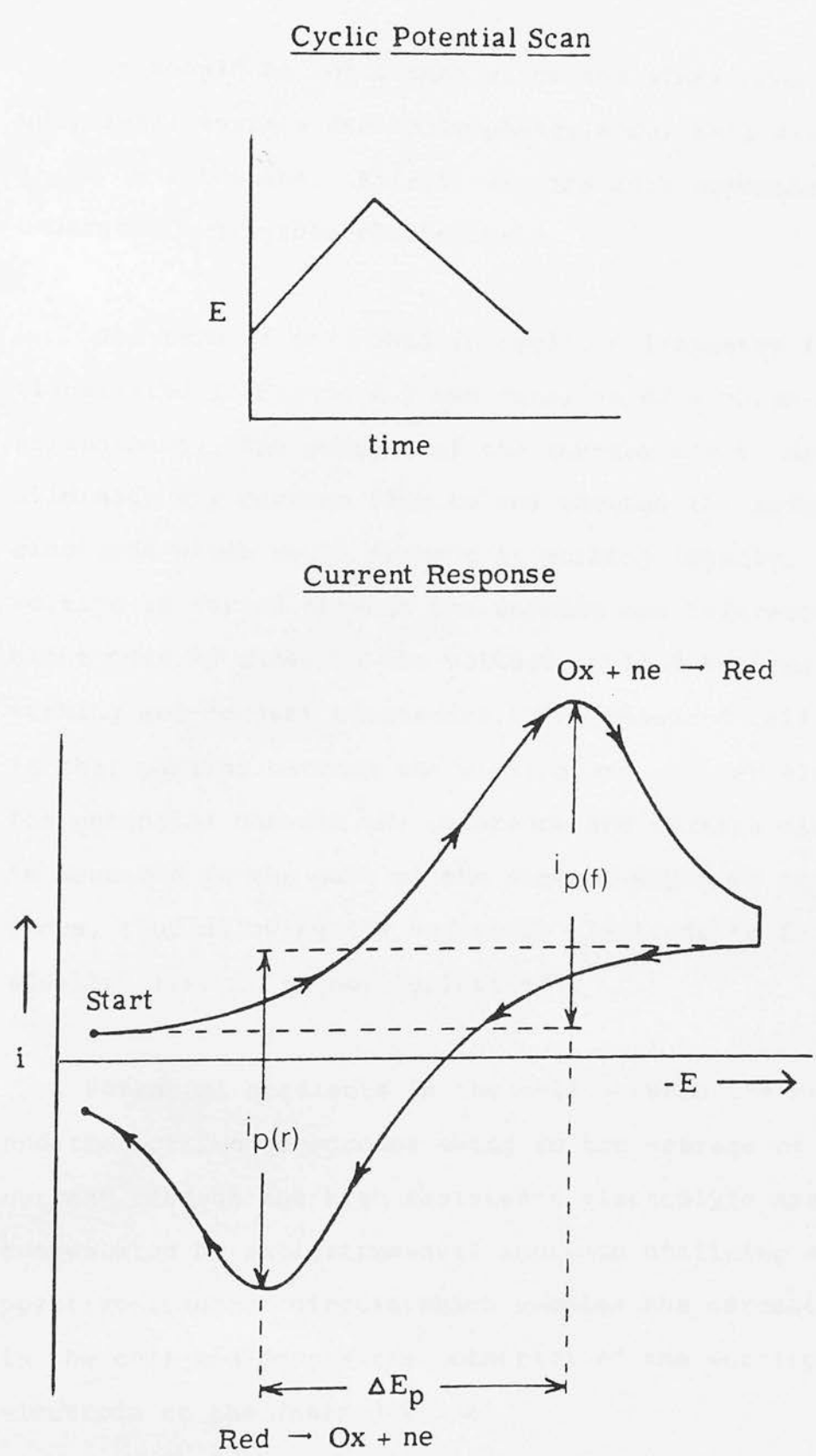
2.1.1.1. Cyclic voltammetry

In linear sweep cyclic voltammetry (c.v.) a stationary electrode is used in a "quiet" (unstirred) solution. This situation is different from that encountered in polarography, where the use of the dropping mercury electrode is equivalent to having an electrode immersed in a totally efficiently stirred solution.

The potential of the electrode is varied linearly with time , the rate at which the potential is changed being the scan rate, ν , (usually 50-500 mVs^{-1}), which effectively controls the time scale of the experiment. The current response is of an asymmetric peaked form, the increase in current occurring when the potential of the electrode is scanned into the range where the reactant begins to be reduced (or oxidised) at the electrode. The rate of this reaction increases rapidly as the potential increases, but soon the electrode reaction has consumed most of the reactant near the electrode surface, in the absence of any stirring action, and the current becomes limited by the rate at which additional reactant can diffuse to the electrode from the bulk of the solution. The current maximum occurs when the tendency towards increasing current, because of the increasingly favourable potential, is just matched by the trend towards decreasing current imposed by the depletion of the reactant near the electrode surface. Beyond the peak the latter of these effects predominates. Upon reaching a pre-set value, the "switching potential", the voltage scan is reversed to its base potential at the same rate used in the forward scan (Figure 2.1).

The complete current wave form for a fully reversible process is of a certain symmetry such that the net current for the forward curve ($i_{p(f)}$) is equal to that for the reverse curve ($i_{p(r)}$) and the peaks are symmetrically displaced from the $E_{\frac{1}{2}}$ value, giving $E_{\frac{1}{2}} = \frac{E_{p(f)} + E_{p(r)}}{2}$

Figure 2.1. Cyclic Voltammetry



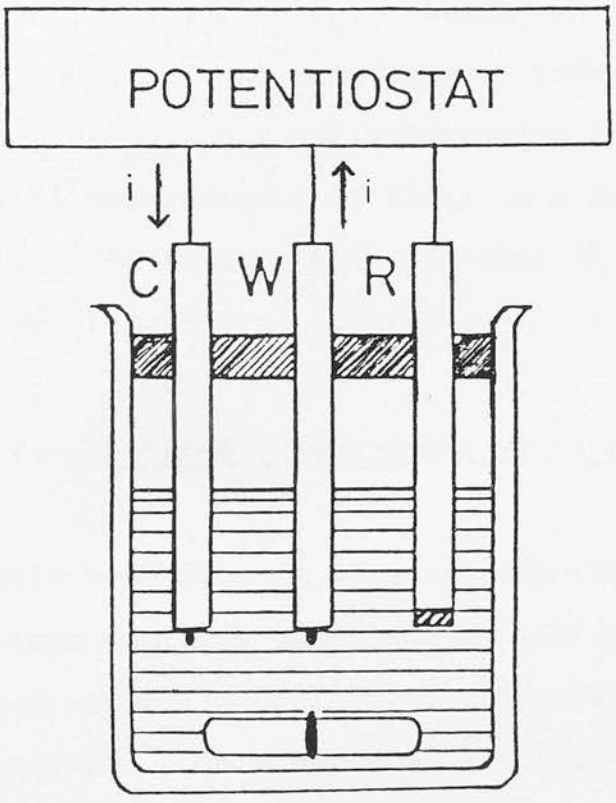
where $E_{p(f)}$ and $E_{p(r)}$ are the forward and reverse peak potentials respectively.

It should be noted that since the electrodes have a very small surface area only μA-scale currents will flow in 10^{-3}M solutions. Effectively the bulk concentration undergoes negligible electrolysis.

The type of cell used in cyclic voltammetry is illustrated in Figure 2.2 and consists of a three-electrode arrangement. The purpose of the counter electrode is to eliminate any current flow to and through the reference electrode which would prevent it working ideally. The voltage is varied between the working and reference electrodes by altering the voltage applied between the working and counter electrodes. The measured cell current is that passing between the working and counter electrodes. The potential between the reference and working electrodes is measured in the part of the circuit where no net current flows, thus allowing the reference electrode to function ideally, i.e. it is not "polarised".

Potential gradients in the cell between the reference and the working electrodes owing to the passage of the cell current through the high resistance electrolyte are compensated by an instrumental approach utilising a positive-feedback circuit which samples the current flowing in the cell and boosts the potential of the working electrode to the desired value.

Figure 2.2. Three-Electrode Apparatus



C, counter electrode

W, working electrode

R, reference electrode

It is important to establish whether or not a particular electrode process is both diffusion limited and fully reversible (i.e. rapid electron transfer in both directions) and simple criteria are available to test these features. These are summarised below:

E_p is independent of ν

$E_{p(f)} - E_{p(r)} = 59/n$ mv and is independent of ν

$\frac{1}{2}[E_{p(f)} + E_{p(r)}] = E_{\frac{1}{2}}$, independent of concentration.

$i_p / \nu^{\frac{1}{2}}$ (current function) is independent of ν

$i_{p(r)} / i_{p(f)} = 1$ and independent of ν

(All measurements at 298K; n = number of electrons involved in the redox process; ν = scan rate in mVs^{-1}).

2.1.1.2. Stirred linear sweep voltammetry

This technique is of great importance since it allows oxidations (current under i = o line) and reductions (current above i = o line) of electroactive species to be distinguished. An example of a stirred and unstirred voltammogram of a species which undergoes both a reversible oxidation and a reversible reduction is shown in Figure 3.1 (Chapter 3).

2.1.1.3. Linear sweep a.c. voltammetry

This technique involves the superposition of a small alternating potential upon a linearly scanning d.c.

potential. The net alternating current component is recorded as a function of the linear d.c. potential and, for a reversible redox step, the output current signal thus recorded is a symmetric peak, centred upon $E_{\frac{1}{2}}$ of the corresponding d.c. polarogram. The additional variable, ω, the a.c. frequency, effectively controls the time-scale of the experiment and provides a particularly sensitive test of departure from reversibility. The criteria for reversibility in linear sweep a.c. volatammetry are given below.

$E_p = E_{\frac{1}{2}}$ (d.c.), independent of concentration and ω.
The wave is highly symmetric with a width at half height of 90mV.
$i_p/\omega^{\frac{1}{2}}$ gives a linear plot which passes through the origin.

Because of the differing phase relationships which the "faradic" and "capacitative" current components have with the applied voltage a.c. voltammetry is able to discriminate against the background "residual" or "capacitative" current. This increases the sensitivity to 10^{-6} or 10^{-7}M solutions. The resolution in a.c. voltammetry is such that waves with a separation of 0.08V can be distinguished, compared with the 0.15V necessary for cyclic voltammetry.

2.2. Synthesis of $Ru_2Cl_4(PMe_2Ph)_5$

As will be shown in later sections of this chapter,

the nature of the phosphine in the systems of type $Ru_2Cl_4(PR_3)_5$ has a profound effect upon the ability of Tl^+ to abstract terminal chloride, and on the ability of the reactive ligand-deficient species formed on chloride abstraction to coordinate alkenes, alkynes etc. It was thought desirable to consolidate the initial useful results obtained with $Ru_2Cl_4(PEt_2Ph)_5$ by studying related systems with similarly basic phosphines. The complex $Ru_2Cl_4(PMe_2Ph)_5$ promised to be one such system.

According to the literature, $Ru_2Cl_4(PMe_2Ph)_5$ has been prepared by reduction of mer-$RuCl_3(PMe_2Ph)_3$ with zinc amalgam in CH_2Cl_2 and isolated as a green-brown solid.[91] Attempts to repeat this reaction are generally unsuccessful and the solid isolated from the reaction consists almost entirely of the cationic complex $[Ru_2Cl_3(PMe_2Ph)_6]Cl$, with very little of the desired neutral species being formed. The cationic species is also formed when the momomer cis-$RuCl_2(PMe_2Ph)_4$ is heated in non-polar solvents, unlike the reactions of $RuCl_2(PPh_3)_3$ with the phosphines PEt_2Ph, $PEtPh_2$ and $PClPh_2$ which give the neutral $Ru_2Cl_4(PR_3)_5$ species via the monomers $RuCl_2(PR_3)_3$.

The preference for the ionic hexakis-phosphine binuclear species is probably due to the particular high strength ascribed to the Ru-P bond for PMe_2Ph. Accordingly, photolysis was considered as a means of cleaving this bond.

2.2.1. Photolysis of cis-$RuCl_2(PMe_2Ph)_4$

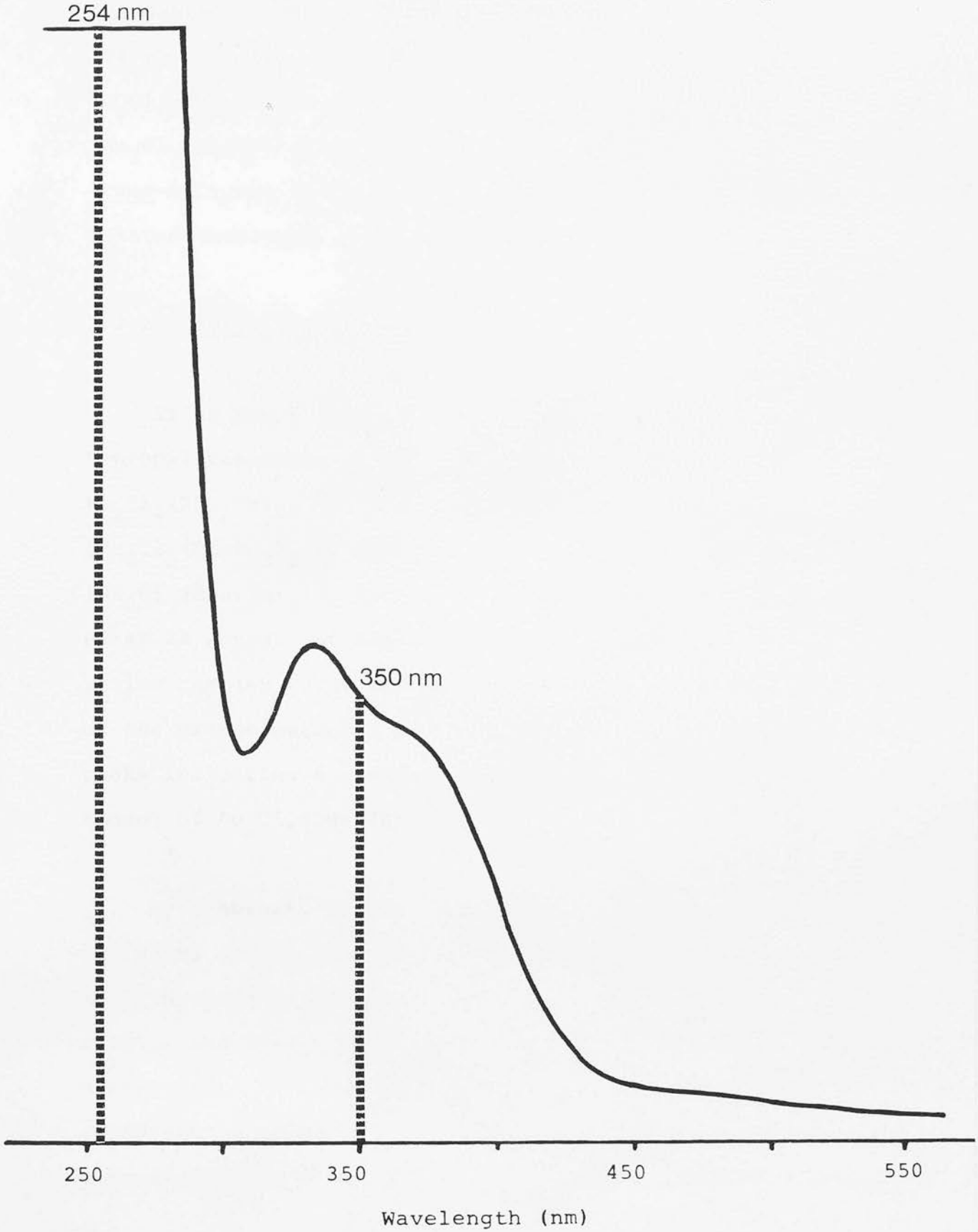
The electronic spectrum of cis-$RuCl_2(PMe_2Ph)_4$ in CH_2Cl_2 shows a very intense absorption in the region of 250nm, presumably due to a metal -> phosphine charge transfer and/or an intra-ligand electronic transition (Figure 2.3). Irradiation of a suspension of yellow cis-$RuCl_2(PMe_2Ph)_4$ in benzene or toluene at 254 nm over a period of 2 to 3 hours gives a clear yellow-orange solution from which the complex $Ru_2Cl_4(PMe_2Ph)_5$ can be isolated in 50-75% yield as an orange powder (in contrast to the green-brown solid reportedly obtained from the reduction of mer-$RuCl_3(PMe_2Ph)_3$). The familiar $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ is also produced in small quantities, but the products are readily separated, one being ionic and the other neutral.

The $^{31}P-[^1H]$ n.m.r. spectrum of $Ru_2Cl_4(PMe_2Ph)_5$ consists of a singlet at δ31.0 p.p.m. and an AB_2 pattern (δ_A 22.7 p.p.m., δ_B 20.4 p.p.m., J_{AB} = 96.3 Hz) with an integral ratio of 2:3.

This photo-reaction is wavelength dependent, since at 350 nm cis-$RuCl_2(PMe_2Ph)_4$ is converted quantitatively to the trans-isomer ($^{31}P-[^1H]$ n.m.r. singlet at δ - 8.6 p.p.m. in C_6D_6). This conversion can be associated with the absorbances at 334 and 370 nm in the electronic spectrum of the cis-isomer, which are probably due to bond weakening d - d transitions (t_2 -> e). Photo-induced cis-trans isomerisations of this type are well known.[92]

Figure 2.3.

Electronic spectrum of cis-$RuCl_2(PMe_2Ph)_4$ in CH_2Cl_2.



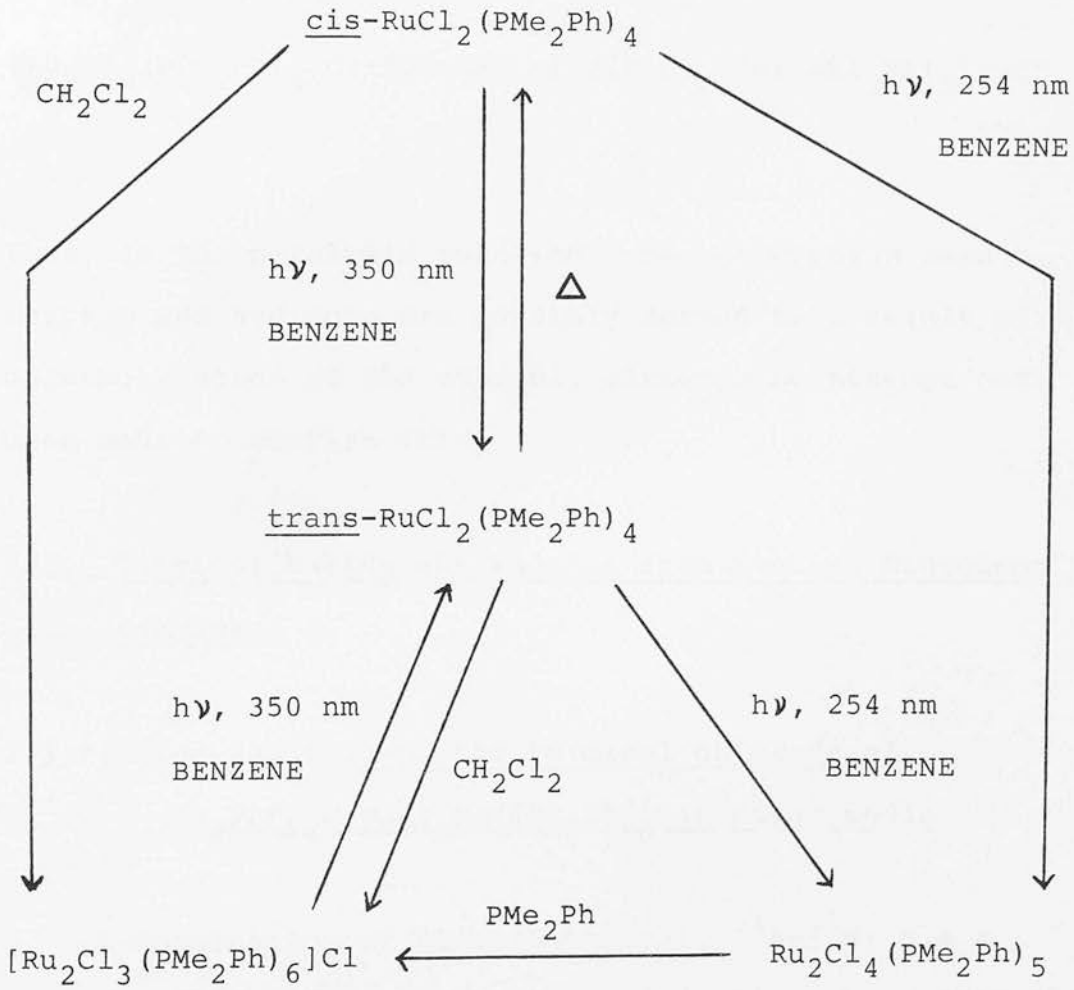
Trans-$RuCl_2(PMe_2Ph)_4$ is converted back to the cis-isomer in solution on heating. When the trans-isomer is subsequently irradiated at 254 nm it yields the same product as direct 254 nm irradiation of the original cis-isomer i.e. $Ru_2Cl_4(PMe_2Ph)_5$. Interestingly the ionic species $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ also gives high yields of trans-$RuCl_2(PMe_2Ph)_4$ when irradiated at 350 nm. These and related observations are summarised in Scheme 2.1.

2.2.2. Pyrolysis of $[Ru_2Cl_3(PMe_2Ph)_6]Cl$

It is known that pyrolysis of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in n-propylpropionate at 393K gives the neutral complex $Ru_2Cl_4(PEt_2Ph)_5$.[68,74,75] Similarly pyrolysis of $[Ru_2Cl_3(PMePh_2)_6]Cl$ gives $Ru_2Cl_4(PMePh_2)_5$. However, when $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ is heated at 400K no change is observed after 24 hours. At higher temperatures (ca 525K) the yellow complex turns orange. The $^{31}P-[^1H]$ n.m.r. spectrum of the orange material in $CDCl_3$ shows a large number of peaks indicating a mixture of species, including a small amount of $Ru_2Cl_4(PMe_2Ph)_5$.

By contrast, if the pyrolysis at ca 525K is carried out using $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ contaminated with ethanol (e.g. derived by boiling $RuCl_2(PPh_3)_3$ with PMe_2Ph in ethanol and merely drying the product in air), the known complex $RuCl_2(CO)(PMe_2Ph)_3$ is obtained in almost quantitative yield. This product has cis-chlorides and a mer-arrangement of PMe_2Ph groups. This reaction is very

Scheme 2.1 Photolytic and related reactions of $RuCl_2(PMe_2Ph)_4$



similar to that of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ to decarbonylate aldehydes to give $RuCl_2(CO)(PEt_2Ph)_3$ and alkenes or alkanes as shown in Equations 2.1 and 2.2. [93,94]

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl+4C_3H_7CHO \rightarrow 2[RuCl_2(CO)(PEt_2Ph)_3] +2C_3H_6+2C_3H_7CH_2OH \quad \ldots \quad 2.1$$

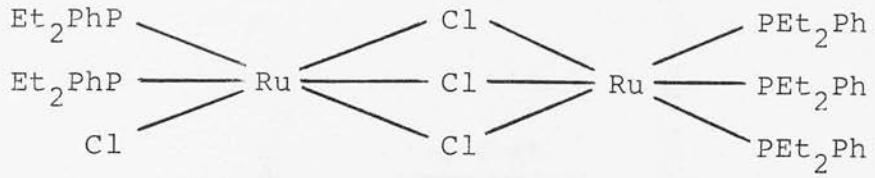
$$[Ru_2Cl_3(PEt_2Ph)_6]Cl+2CH_3CHO \rightarrow 2[RuCl_2(CO)(PEt_2Ph)_3]+2CH_4 \quad \ldots \quad 2.2$$

Thus, in the pyrolysis reaction under discussion here methane and hydrogen are possibly formed as a result of decarbonylation of the ethanol, although no attempt has been made to confirm this.

2.3. Terminal halide abstraction from neutral binuclear complexes

2.3.1. The lability of the terminal chloride of $(Et_2PhP)_2ClRuCl_3Ru(PEt_2Ph)_3$ in polar media

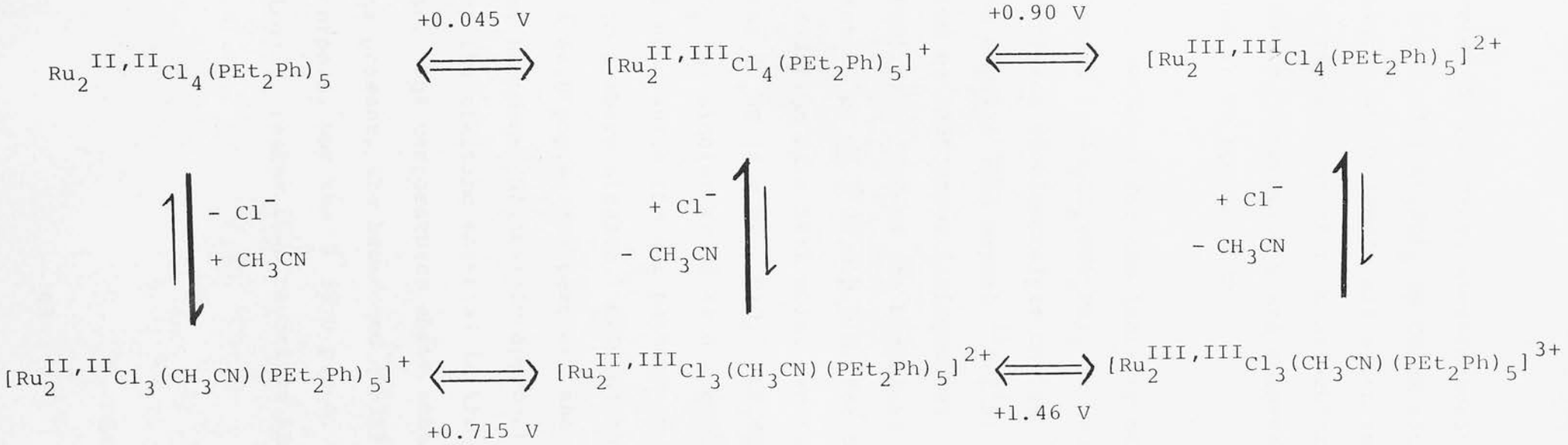
A combination of electrochemical, ^{31}P-$[^1H]$ n.m.r. spectroscopic and conductivity studies have shown that the terminal chloride ligand in the complex $Ru_2Cl_4(PEt_2Ph)_5$ (20) is surprisingly labile in varied polar media.



(20)

An a.c. voltammogram of $Ru_2Cl_4(PEt_2Ph)_5$ in CH_2Cl_2/Bu_4NBF_4 (0.5M) shows two reversible oxidations at +0.04 and +0.90V (vs.Ag/Ag^+). The first of these oxidations is localised on the "harder" terminal-chloride-bearing metal centre and the second on the adjacent "soft" ruthenium atom of the binuclear unit. In CH_3CN, the first oxidation ($Ru_2(II,II)$ -> $Ru_2(II,III)$) shifts dramatically to +0.71V and this is attributed to spontaneous replacement of terminal chloride by CH_3CN to give the cation $[Ru_2Cl_3(CH_3CN)(PEt_2Ph)_5]^+$. Although the conversion to the solvato complex is complete after only a few minutes the return scan of the a.c. voltammogram shows only a small wave corresponding to reduction of the dication $[Ru_2Cl_3(CH_3CN)(PEt_2Ph)_5]^{2+}$, and a major wave corresponding to reduction of the $Ru_2(II,III)$ species $[Ru_2Cl_4(PEt_2Ph)_5]^+$. This is due to preferential replacement of the neutral CH_3CN ligand by free chloride (still present in solution) at the ruthenium (III) centre once oxidation of the neutral species has occurred. By adding $NaBF_4$ to the solution of $Ru_2Cl_4(PEt_2Ph)_5$ in CH_3CN, free chloride ion is removed; then only the processes associated with the CH_3CN complex are observed in both the forward and return waves of the a.c. voltammogram. This behaviour is summarised in Scheme 2.2.

Scheme 2.2. Electrochemical behaviour of $Ru_2Cl_4(PEt_2Ph)_5$ in CH_3CN



E(V) vs. Ag/Ag^+ in CH_3CN

As expected from these electrochemical studies, fresh solutions of $Ru_2Cl_4(PEt_2Ph)_5$ in CH_3CN show a gradual rise in conductivity which levels off after several minutes, ascribed to replacement of terminal-chloride by CH_3CN. Similar rises in conductivity are observed when the complex is dissolved in CH_3NO_2 or MeOH.

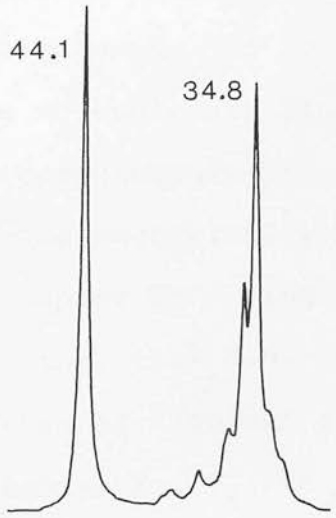
Further evidence for the lability of the terminal chloride ligand in $Ru_2Cl_4(PEt_2Ph)_5$ is provided by the unexpected effect of electrolyte on its $^{31}P-[^1H]$ n.m.r. spectrum in CD_2Cl_2. The normal $^{31}P-[^1H]$ n.m.r. spectrum of this complex at 293K shows a singlet at δ 44.0 p.p.m. for the "$(Et_2PhP)_2ClRu$" end of the binuclear unit and an AB_2 pattern centred at ca δ 35.0 p.p.m. for the "$Ru(PEt_2Ph)_3$" end. On addition of a 50:1 molar excess of any of the electrolytes Bu_4NX ($X = BF_4^-, ClO_4^-, CF_3SO_3^-, BPh_4^-, PF_6^-$) or Et_4NClO_4 the singlet at δ 44.0 p.p.m. is broadened to a very small hump while the AB_2 pattern at δ 35.0 p.p.m. collapses to a sharp singlet. On cooling the solution, the signal at δ 44.0 p.p.m. sharpens and the signal at 35.0 p.p.m. broadens, ultimately approaching (at 203K) the spectrum of the starting material in the absence of electrolyte. For temperatures above ambient with electrolyte present, the broadened (293K) δ 44.0 p.p.m. singlet sharpens, but the δ 35.0 p.p.m. resonance remains a sharp singlet, rather than revealing AB_2 character (Figure 2.4).

Figure 2.4.

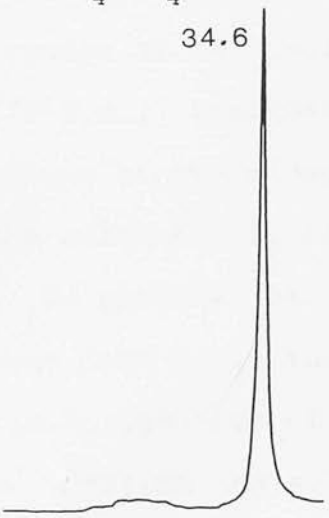
The effect of electrolyte on $^{31}P-[^{1}H]$ n.m.r. spectrum of $Ru_2Cl_4(PEt_2Ph)_5$

CH_2Cl_2 solution with C_6D_6 capillary lock

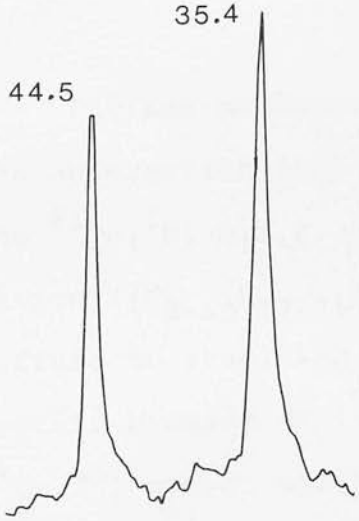
(i) $Ru_2Cl_4(PEt_2Ph)_5$ at 293K



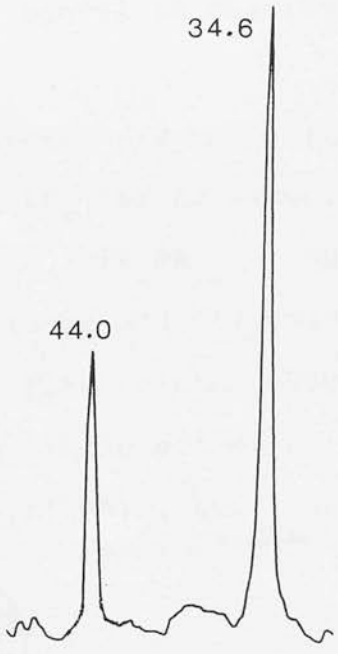
(ii) 50:1 molar excess of Bu_4NBF_4 added (293K)



(iii) Solution containing electrolyte at 223K



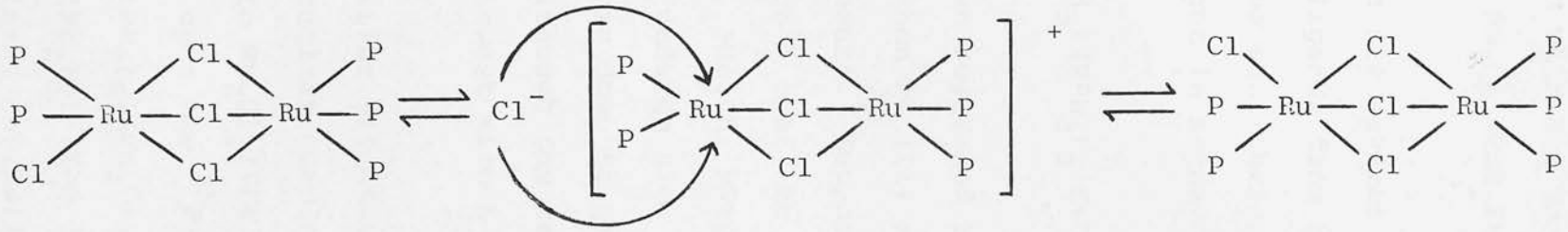
(iv) Solution containing electrolyte at 309K



These observations suggest that in the presence of added electrolyte the terminally coordinated chloride ion is released and stabilised to some extent by ion-pair association with the high concentration of tetra-alkyl ammonium cations. The process is a dynamic one at ambient temperature; the chloride ion rapidly leaving and recombining with the metal centre. The recombination need not occur on the same "side" as that previously occupied by the chloride ion so that the PEt_2Ph groups at that end of the molecule are fluxional and the ^{31}P n.m.r. resonance is correspondingly broad. The PEt_2Ph groups at the other end become magnetically equivalent and the original AB_2 pattern collapses to a singlet (Figure 2.5). On progressive cooling, this dynamic process is slowed down until the system is "frozen" and the characteristic spectrum of the original $Ru_2Cl_4(PEt_2Ph)_5$ is observed. Heating the solution above ambient temperature increases the rate of the dynamic process to such an extent that the signal at δ 44.0 p.p.m. sharpens. In this case however, the PEt_2Ph groups giving rise to the signal at δ 35.0 p.p.m. remain magnetically equivalent and no broadening of the signal is observed.

Further evidence for this phenomenon is provided by the observation that bulky "adogen" BF_4 has no effect on the $^{31}P-[^1H]$ n.m.r. spectrum of $Ru_2Cl_4(PEt_2Ph)_5$. Here the cation ($[C_{8-10}H_{17-21}]_3MeN^+$) is too large and its charge too diffuse to stabilise chloride ion. Electrolytes which contain bromide or iodide also have little effect on the $^{31}P-[^1H]$ n.m.r. spectrum of $Ru_2Cl_4(PEt_2Ph)_5$, and those

Figure 2.5. Fluxional behaviour of $Ru_2Cl_4(PEt_2Ph)_5$ in electrolyte solution (CD_2Cl_2)



P = PEt_2Ph

containing chloride have no effect. This is to be expected since in these cases the cation is already closely associated with the small halide ion, removing the driving force for $Ru_2Cl_4(PEt_2Ph)_5$ to dissociate.

There are several precedents for dissociation of chloride ligands from ruthenium (II) complexes in polar media. The equilibrium shown in Equation 2.3 lies largely to the right in methanol.[95]

$$RuCl(\eta\text{-}C_5H_5)(PPh_3)_2 + MeOH \rightleftharpoons [Ru(MeOH)(\eta\text{-}C_5H_5)(PPh_3)_2]Cl \quad \ldots 2.3$$

It has been suggested that this is likely to be a general reaction when Ru (II) species of this type are dissolved in donor solvents. Support for this comes from the observation[96] that the complexes $RuCl(\eta\text{-}C_5H_5)(L)_2$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$, $P(OMe)Ph_2$, $PMe(OMe)_2$ and L_2 = dppe) all undergo slow solvolysis of chloride ion when dissolved in dmso to give the $[Ru(dmso)(\eta\text{-}C_5H_5)(L)_2]^+$ cation, although the rates of solvolysis vary enormously with L (slowest with $L = PMe(OMe)_2$, fastest with $L = PMe_3$).

A similar situation i.e. L - dependence, is observed in the binuclear complexes under study here, since in contrast to $Ru_2Cl_4(PEt_2Ph)_5$ the presence of electrolyte has no effect upon the $^{31}P\text{-}[^1H]$ n.m.r. spectra of $Ru_2Cl_4(PEtPh_2)_5$, $Ru_2Cl_4(Y)(PPh_3)_4$ (Y = CO,CS) or $Ru_2Cl_4(PClPh_2)_5$. The influence of the neutral ligands in such complexes on lability of terminal chloride ligands

will be discussed more fully below (Sections 2.3.2.3. to 2.3.2.10).

Attempts to isolate the cations $[Ru_2Cl_3(L)(PEt_2Ph)_5]^+$ (L = CH_3CN, MeOH, CH_3NO_2) from solutions of $Ru_2Cl_4(PEt_2Ph)_5$ in the relevant solvent have been unsuccessful. ^{31}P n.m.r. studies of such solutions have shown that although the solvated cations are formed fairly rapidly at room temperature this is soon followed by bridge cleavage reactions to give mixtures of unidentified species, presumably monomeric. Considerably greater success in preparing these species follows from the techniques described in the next section.

Finally, when solutions of $Ru_2Cl_4(PEt_2Ph)_5$ in non-coordinating solvents such as CH_2Cl_2 are treated with alkenes or alkynes no evidence of displacement of terminal chloride by these potential ligands has been observed.

2.3.2. Terminal halide abstraction using $TlBF_4$

As described below, terminal halide abstraction from various triple-halide-bridged binuclear ruthenium (II) complexes has been most effectively achieved using $TlBF_4$. Other halide-abstracting agents such as $NaBF_4$, $NaBPh_4$, $AgBF_4$ and NH_4PF_6 were found to be less effective. In addition it is suspected that Ag(I) salts may take part in alternative reactions which are undesirable in this context (see Chapter 6).

2.3.2.1. The reactions of $Ru_2Cl_4(PEt_2Ph)_5$

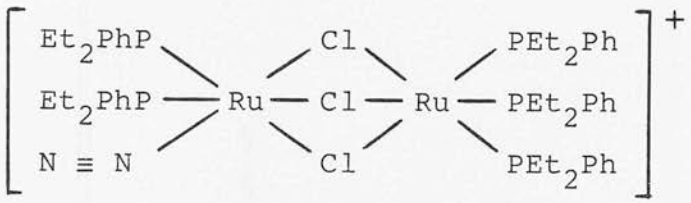
2.3.2.1.1. Formation of $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$

When a CH_2Cl_2 solution of the complex $Ru_2Cl_4(PEt_2Ph)_5$ is stirred with an equimolar amount of $TlBF_4$ under an atmosphere of N_2 at ambient temperature for 3 hours, a colour change from orange to light yellow-brown is observed. Concentration of the solution after filtering off the fine precipitate of TlCl gives a light brown oil which on trituration with n-hexane is converted to a mustard coloured powder. Conductivity studies on a CH_2Cl_2 solution of this product over a range of concentrations show it to be a 1:1 electrolyte. The i.r. spectrum shows a strong band at 2140 cm^{-1} assigned to terminally bound $\nu_{N \equiv N'}$ a broad band centred at 1040 cm^{-1} due to the BF_4^- counter-ion and a bridging ν_{Ru-Cl} band at 255 cm^{-1}. The absence of a terminal ν_{Ru-Cl} band is a good indication of terminal chloride abstraction. The shift to lower frequency of $\nu_{N \equiv N}$ on coordination, from 2330 cm^{-1} for molecular N_2 (Raman), is in agreement with back- donation of electron density from the metal centre to the π^* anti-bonding orbitals of the N_2.

Analysis figures for this solid are somewhat variable due to the tendency of the cationic complex to lose N_2 when removed from an atmosphere of N_2 but are reasonably consistent with the formulation $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$.

The $^{31}P-[^{1}H]$ n.m.r. spectrum of this dinitrogen species shows evidence of some form of ligand fluxionality or exchange at ambient temperature. Considerable spectral improvement occurs at 218K, giving a singlet at δ 37.1 p.p.m. and a well resolved AB_2 pattern (δ_A 36.6 p.p.m., δ_B 35.5 p.p.m., J_{AB}=34.1 Hz; Figure 2.6).

This data is very good evidence for the proposed cation having structure (21).



(21)

The broad nature of the $^{31}P-[^{1}H]$ n.m.r. resonances at ambient temperature is probably due to reversible dissociation of the N_2 ligand.

The shift in the position of the singlet resonance associated with the PEt_2Ph groups attached to the ruthenium centre where terminal chloride is replaced by dinitrogen (from δ 44.0 to δ 37.1 p.p.m.) is consistent with the replacement of an anionic ligand by a neutral one. As might be expected, there is little change in the position of the AB_2 pattern associated with the PEt_2Ph groups on the remote metal centre.

Figure 2.6.

$^{31}P-[^{1}H]$ n.m.r. spectrum of $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ in $CDCl_3$.

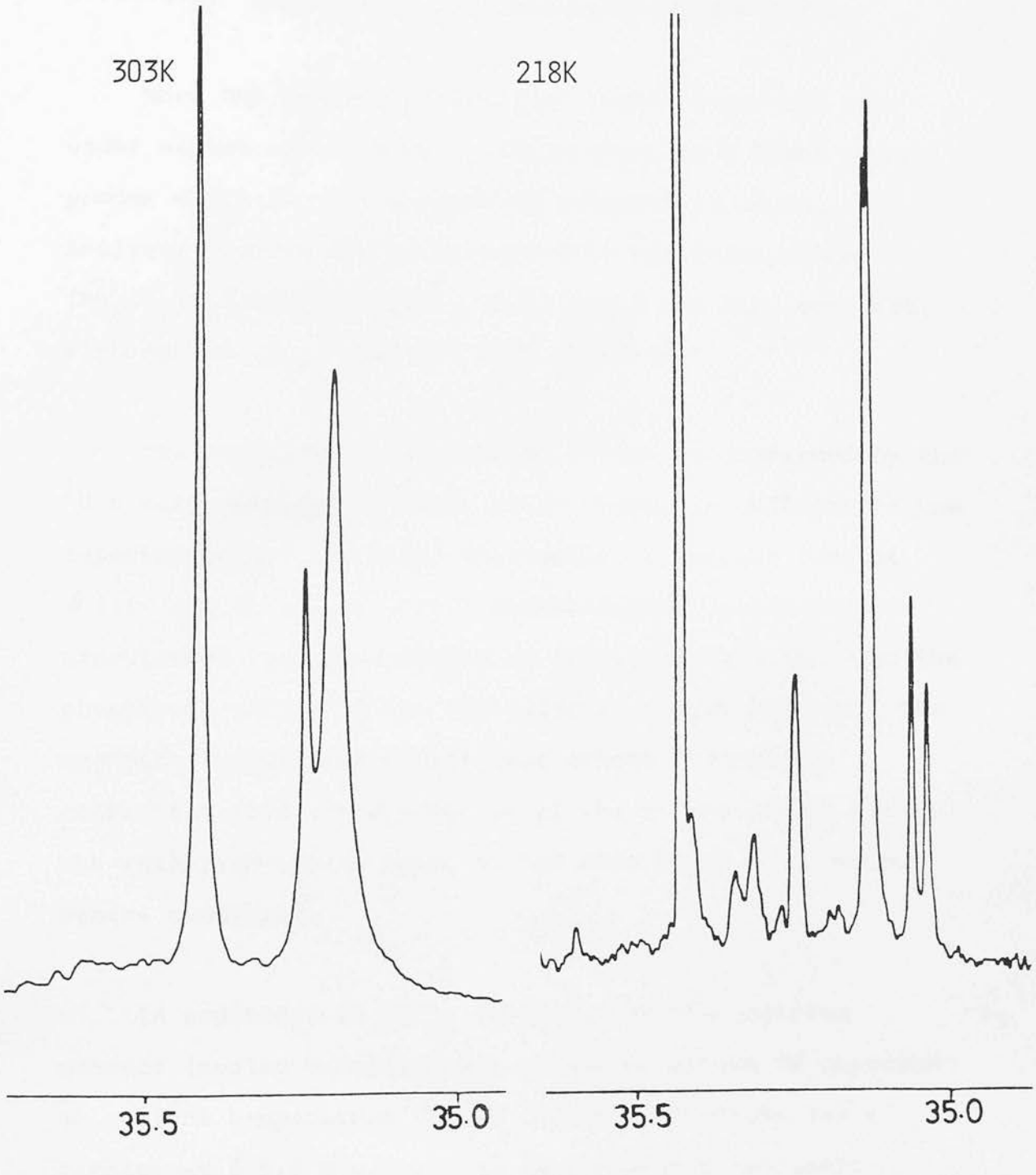


Table 2.1 gives the $^{31}P-[^{1}H]$ and ^{1}H n.m.r. data as well as selected i.r. bands for the new cations $[Ru_2Cl_3(L)(PR_3)_5]^+$ described in this chapter.

2.3.2.1.2. Formation of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$

When the procedure described above is carried out under ethene rather than N_2 the product is a light orange powder which forms a conducting solution in CH_2Cl_2. Analysis figures are consistent with the formulation $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22), as is the i.r. spectrum, although no $\nu_{C=C}$ band has been observed.

The presence of coordinated ethene is confirmed by the ^{1}H n.m.r. spectrum in $CDCl_3$ which shows, in addition to the expected phenyl and ethyl resonances, a triplet (4H) at δ 3.14 p.p.m. (J_{PH}=2.0Hz), Heteronuclear decoupling experiments confirm coupling of the ethene protons with the phosphorus nuclei of the two adjacent PEt_2Ph ligands. The magnetic equivalence of all four ethene protons is consistent with rapid rotation of the ethene ligand around the ruthenium-ethene axis, as has been found for numerous ethene complexes.

In addition, in $CDCl_3$ solutions of the isolated product (sealed under vacuum) some free ethene is observed at ambient temperature in the ^{1}H n.m.r. spectrum (as a singlet at δ 5.4 p.p.m.), indicating some dissociation of the complex. In cooled solutions the amount of free ethene

Table 2.1. $^{31}P-[^{1}H]$ and ^{1}H n.m.r. data for the compounds $[Ru_2X_3(L)(PR_3)_5]BF_4$ with selected i.r. bands

Compound	$\delta\,^{31}P-[^{1}H]$(p.p.m.)		$\delta\,^{1}H$(p.p.m.)[e]	Assignment	i.r.(cm^{-1})	Assignment
	Singlet	AB_2				
$[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ (21)	37.1[a]	δ_A36.6; δ_B35.5 (J_{AB}34.1Hz)	-	-	2140	$\nu_{N\equiv N}$
$[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22)	35.1[b]	δ_A38.9; δ_B36.2	3.2(t) (J_{PH}2.0Hz)	$C_2\underline{H}_4$	-	-
$[Ru_2Cl_3(PhC_2H)(PEt_2Ph)_5]BF_4$ (23)	33.6[a]	36.2,36.3[d]	4.7(t) (J_{PH}3-7Hz)	$PhC_2\underline{H}$	1972 3310	$\nu_{C\equiv C}$ ν_{C-H} (alkyne)
$[Ru_2Cl_3(dmac)(PEt_2Ph)_5]BF_4$ (24)	28.0[b]	37.4,36.2[d]	3.3-3.9	CH_3(dmac)	1880 1720	$\nu_{C\equiv C}$ $\nu_{C=O}$
$[Ru_2Cl_3(CH_3CN)(PEt_2Ph)_5]BF_4$ (25)	41.8[b]	δ_A35.7; δ_B35.0 (J_{AB}31.0Hz)	-	-	2270	$\nu_{C\equiv N}$
$[Ru_2Cl_3(CH_3NO_2)(PEt_2Ph)_5]BF_4$ (26)	41.5[b]	δ_A35.3; δ_B34.8 (J_{AB}31.0Hz)	-	-	1550 1350	$\nu_{N=O}$
$[Ru_2Cl_3(CH_2CHCl)(PEt_2Ph)_5]BF_4$ (27)	34.1[c]	35.5[d]	-	-	1605 608	$\nu_{C=C}$ ν_{C-Cl}

Table 2.1. (continued)

Compound	$\delta^{31}P-[^1H]$(ppm)		δ^1H(ppm)	Assignment	i.r.(cm^{-1})	Assignment
	Singlet	AB_2–				
$[Ru_2Br_3(N_2)(PEt_2Ph)_5]BF_4$	37.5[a]	δ_A36.0; δ_B35.1 (J_{AB}30.6Hz)	–	–	2145	$\nu_{N\equiv N}$
$[Ru_2Br_3(C_2H_4)(PEt_2Ph)_5]BF_4$	35.0[b]	δ_A40.0, δ_B36.3 (J_{AB}34.5Hz)	3.2(t) (J_{PH}2.0Hz)		–	–
$[Ru_2Cl_3(C_2H_4)(PEtPh_2)_5]BF_4$[f]	36.0[a]	37.8[d]	3.2(t) (J_{PH}2.0Hz)	C_2H_4	–	–

a 220K, b 230K, c 213K, d poorly resolved, e ambient temperature, f impure product, (t) triplet

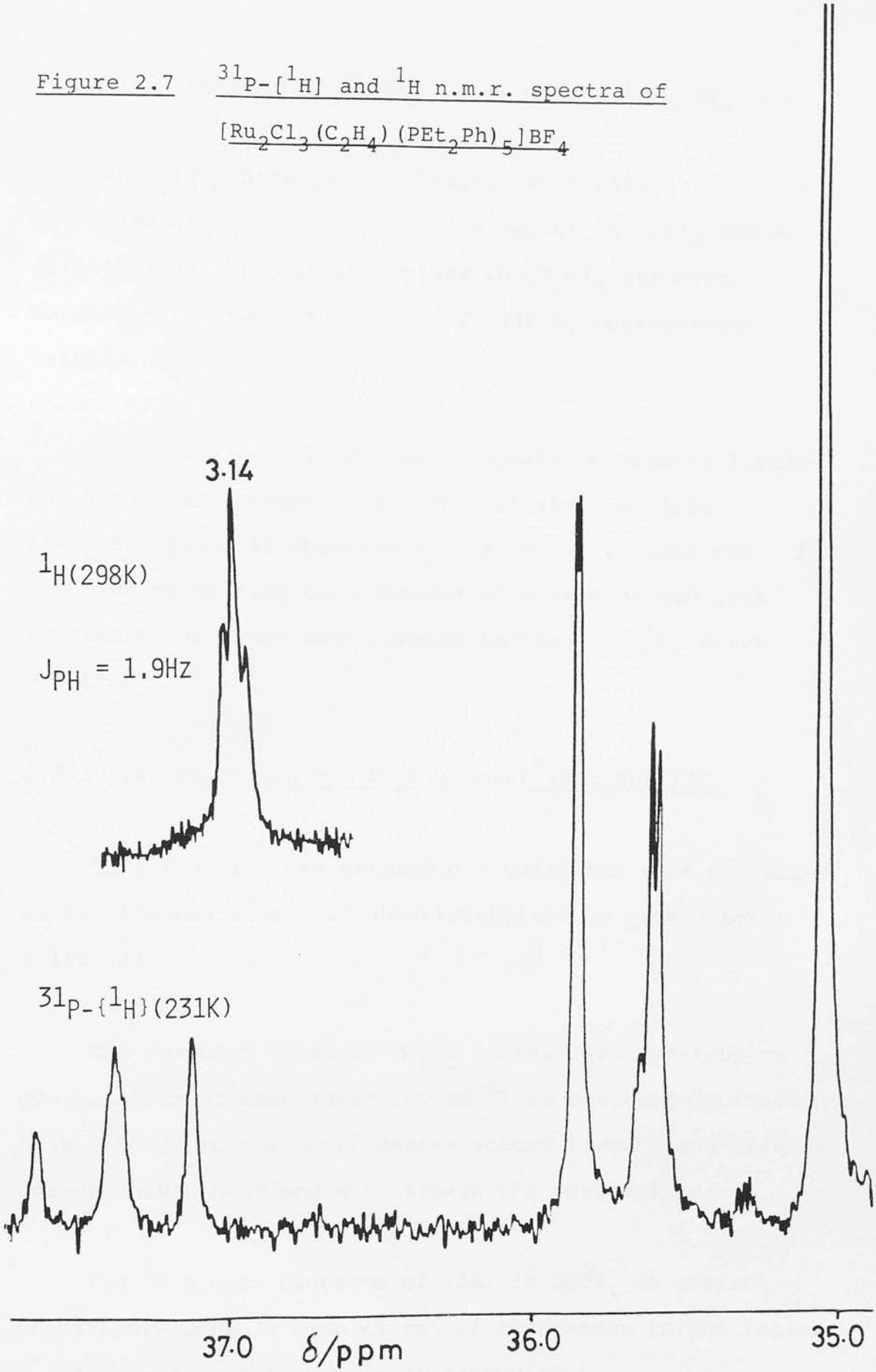
All n.m.r. data were obtained using $CDCl_3$ or CD_2Cl_2 solutions.

i.r. spectra were recorded using Nujol mulls.

decreases while the intensity of the coordinated ethene signal increases, showing that the dissociation of ethene is reversible. An alternative explanation for the magnetic equivalence of the ethene protons involving a dissociative process seems unlikely, since such efficient exchange would also quench the phosphorus coupling.

As with the dinitrogen species (21) the $^{31}P-[^{1}H]$ n.m.r. spectrum of the ethene compound at ambient temperature is uninformative, consisting of a singlet at δ 34.7 p.p.m. and two very broad resonances in the region δ 35.0 to 40.0 p.p.m. At 234K however, the expected spectrum is observed i.e. a singlet at δ 35.1 p.p.m. and an AB_2 pattern (δ_A 38.9 p.p.m., δ_B 36.2 p.p.m., J_{AB}=34.2Hz, Figure 2.7). Interestingly in this case the singlet associated with the PEt_2Ph groups adjacent to the ethene ligand occurs at lower frequency than the AB_2 pattern for the three remote PEt_2Ph groups. This contrasts with the situations in the starting material and the dinitrogen species (21) in which the singlets are at higher frequencies than the relevant AB_2 patterns. This may be seen as a progressive shift of the "$(PEt_2Ph)_2L$" resonance with decreasing electron density ($L = \overrightarrow{Cl^-, N_2, C_2H_4}$) on the Ru(II) centre (due to the increasing π-acceptor ability of L). The AB_2 pattern for the ethene species is itself interesting in that it is almost first order (AX_2).

Figure 2.7 $^{31}P-[^{1}H]$ and ^{1}H n.m.r. spectra of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$



2.3.2.1.3. Formation of $[Ru_2Cl_3(PhC_2H)(PEt_2Ph)_5]BF_4$ (23)

The light brown solid obtained by treating $Ru_2Cl_4(PEt_2Ph)_5$ with an equimolar amount of $TlBF_4$ and a slight excess of phenylacetylene in CH_2Cl_2 has been formulated as the title compound (23) by conventional methods.

The phenylacetylene ligand appears to be more firmly bound than the ethene ligand in (22) since no free phenylacetylene is observed in the ^1H n.m.r. spectrum. At the time of writing the coordinated alkyne carbon atom resonances have not been located in the $^{13}C-[^1H]$ n.m.r. spectrum.

2.3.2.1.4. Formation of $[Ru_2Cl_3(dmac)^*(PEt_2Ph)_5]BF_4$

This reaction was carried out using the same procedure as for the reaction with phenylacetylene to give a brown solid (24).

The dramatic shift of $\nu_{C\equiv C}$ in the i.r. spectrum on coordination of dmac (over 200 cm^{-1}) is a strong indication that binding to the metal centre occurs through the carbon-carbon double bond and not through the carboxyl groups.

The ^1H n.m.r. spectrum of (24) in $CDCl_3$ at ambient temperature shows a complex set of resonances in the region

* (dmac = dimethylacetylenedicarboxylate)

δ3 3 to 3 9 p.p.m. for the methyl groups of the coordinated alkyne suggesting the presence of various isomeric forms of this cation which very probably differ in the orientation of the bulky alkyne. Broad resonances are also observed in the $^{31}P-[^{1}H]$ n.m.r. spectrum.

As for the phenylacetylene complex (23) the alkyne carbon atom resonances of (24) have not been located in the $^{13}C-[^{1}H]$ n.m.r. spectrum.

2.3.2.1.5. Formation of $[Ru_2Cl_3(CH_3CN)(PEt_2Ph)_5]BF_4$ (25)

An important feature in the preparation of this cation is that if more than one molar equivalent of CH_3CN is used bridge cleavage occurs to give a mixture of monomeric species, as was found in the reaction of $Ru_2Cl_4(PEt_2Ph)_5$ in neat CH_3CN (Section 2.3.1.).

2.3.2.1.6. Formation of $[Ru_2Cl_3(CH_3NO_2)(PEt_2Ph)_5]BF_4$ (26)

The $^{31}P-[^{1}H]$ n.m.r. spectrum of this species in $CDCl_3$ is very similar to that of the CH_3CN adduct. In addition, the presence of excess CH_3NO_2 also causes bridge cleavage to give monomers (see above for CH_3CN).

2.3.2.1.7. The reaction with vinyl chloride

Should it be found possible to convert the ethene ligand in $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ to vinyl chloride, the

ease with which the vinyl chloride may be removed from the resulting cationic complex will be of great importance. It was therefore decided to attempt to prepare this species by direct reaction of vinyl chloride with $Ru_2Cl_4(PEt_2Ph)_5$ and $TlBF_4$.

On stirring equimolar amounts of $Ru_2Cl_4(PEt_2Ph)_5$ and $TlBF_4$ in CH_2Cl_2 under an atmosphere of vinyl chloride the solution turns brown-green over a 3 hour period. The brown-green solid isolated from the solution gives a complex $^{31}P-[^1H]$ n.m.r. spectrum in $CDCl_3$ at both ambient and low temperatures suggesting a mixture of species. The ^1H n.m.r. spectrum shows that no vinyl chloride is present. It is thought that under these conditions chloride abstraction from vinyl chloride by Tl^+ occurs so that this route to a vinyl chloride complex is not feasible.

The discovery of N_2/C_2H_4 exchange reactions (see 2.3.1.11 below) suggested an alternative route to the desired vinyl chloride species. When vinyl chloride is allowed to bubble through a solution of the dinitrogen species (21) in CH_2Cl_2 for ca 30 minutes an orange solid can be isolated from the reaction mixture. This product is extremely unstable, tending to give a sticky material which rapidly turns green, even when stored at low temperatures under an atmosphere of vinyl chloride. For this reason no reliable analytical data have been obtained for this solid, which is nonetheless formulated as $[(Et_2PhP)_2(CH_2{=}CHCl)RuCl_3Ru(PEt_2Ph)_3]BF_4$ (27).

The i.r. spectrum of the product is very similar to that of the dinitrogen species from which it was prepared except for the absence of the $\nu_{N\equiv N}$ band at 2140 cm^{-1} and the appearance of a weak band at 1605 cm^{-1} assigned to $\nu_{C=C}$. A shoulder at ca 680 cm^{-1} on one of the tertiary phosphine bands is assigned to ν_{C-Cl} (cf $Rh(acac)(CH_2=CHCl)_2$[97,98] ν_{C-Cl} at 680 cm^{-1}).

The ^1H n.m.r. spectrum of the orange solid dissolved in CD_2Cl_2 shows only free vinyl chloride as an ABC set of resonances in the region δ 5.3 to 6.5 p.p.m., with no evidence for coordinated vinyl chloride. This applies even when the solid is dissolved in CD_2Cl_2 at low temperature and the ^1H n.m.r. spectrum recorded at 223K (below this temperature all the resonances are very broad). Comparison of the integrals for the vinyl chloride resonances with those of the ethyl or phenyl groups of the PEt_2Ph ligands does, however, give a ratio of vinyl chloride to PEt_2Ph very close to 1:5, as expected for the desired species.

The $^{31}P-[^1H]$ n.m.r. spectrum of a CD_2Cl_2 solution of this orange solid at 213K (or lower) consists of a singlet at δ 34.1 p.p.m. and a broad set of resonances at ca δ 35.5 p.p.m. The positions of these resonances are very similar to those observed for the singlet and AB_2 pattern of the ethene species (22) and it would seem likely that they correspond to the desired cationic complex $[Ru_2Cl_3(CH_2=CHCl)(PEt_2Ph)_5]BF_4$ (27). It is important to note that at this temperature (213K), as already mentioned,

the ^{1}H n.m.r. spectrum is broadened and uninformative. After several minutes at 213K two additional sharp peaks are observed in the $^{31}P-[^{1}H]$ n.m.r. spectrum of this solution, at δ43.4 and 35.5 p.p.m. These peaks grow at the expense of the signals assigned to (27) (more rapidly if the solution is warmed up) and they are due to formation of the species $[RuCl_2(PEt_2Ph)]_n$ and $[Ru_2Cl_3(PEt_2Ph)_6]^+$ respectively. These same products are obtained on chloride abstraction from $Ru_2Cl_4(PEt_2Ph)_5$ in the absence of any suitable replacement ligand (see Section 2.3.2.1.10).

These observations suggest that the vinyl chloride species (27) is formed in quantitative yield when vinyl chloride is bubbled through a solution of the dinitrogen species (21). The cationic complex (27) is only stable in solution at low temperatures for short periods in the absence of an excess of vinyl chloride or at ambient temperature when a large excess of vinyl chloride is present. In the former case the coordinated vinyl chloride is irreversibly lost on standing or if the solution is warmed up.

Attempts have been made to prepare the vinyl chloride derivative (27) from the ethene species (22). Thus a solution of (22) in CH_2Cl_2 was treated with vinyl chloride in exactly the same manner. The ^{1}H n.m.r. spectrum of a CD_2Cl_2 solution of the orange solid obtained from this reaction is very similar to that of the product (27) previously described except for the presence of a triplet

resonance at δ 3.1 p.p.m. corresponding to residual coordinated ethene. The estimated proportions of vinyl chloride to ethene is ca 1:1. It therefore seems that although vinyl chloride can displace dinitrogen fairly easily from (21) it is less effective in displacing ethene from (22). This gives some measure of the relative stabilities of the dinitrogen and ethene species.

An interesting observation has been made when the orange vinyl chloride species (27) is exposed to air in the solid state at room temperature. A rapid colour change from orange to green is observed (visually similar to that observed at low temperature under an atmosphere of vinyl chloride, see previously) suggesting partial oxidation of the ruthenium (II) species. However the i.r. spectrum of this mixture shows an intense band at 2140 cm^{-1} which is assigned to $\nu_{N\equiv N}$ of coordinated dinitrogen on ruthenium (II). The intensity of this band gradually decreases on further exposure to air. It would seem that two competing processes take place on exposure of (27) to air, namely, displacement of vinyl chloride by dinitrogen and oxidation of ruthenium (II). It has also been found that if a suspension of the vinyl chloride species (27) in hexane is stirred under dinitrogen for several hours the mustard-yellow dinitrogen species (21) is obtained in high yield.

Although the vinyl chloride complex (27) is relatively unstable this study has been extremely useful. Indeed the lability of this complex may be considered a promising

observation since if conversion of the ethene ligand in (22) to vinyl chloride is achieved it is now known that the vinyl chloride can be easily displaced.

2.3.2.1.8. Reactions with further alkenes and dienes

When a CH_2Cl_2 solution of $Ru_2Cl_4(PEt_2Ph)_5$ under argon is treated with an equimolar amount of $TlBF_4$ and an excess of styrene, propene, butadiene, 1,5-cyclooctadiene or cyclooctatetraene the reaction proceeds as if no replacement ligand were available. The products isolated from the reactions are $[RuCl_2(PEt_2Ph)_2]_n$ and $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$ as identified by ^{31}P n.m.r. and i.r. spectroscopy. The ^1H n.m.r. spectra of the products show no indication of the presence of any of the added alkenes, either coordinated or free. Indeed, if the reactions are carried out under N_2 instead of argon the dinitrogen species (21) is obtained.

It therefore seems that the vacant site in $[Ru_2Cl_3(PEt_2Ph)_5]^+$ is ethene-specific, as far as coordination of alkenes is concerned. Steric constraints to coordination may be proposed for the bulky ligands butadiene, cod and cot, but this seems unlikely to apply to styrene or propene, particularly when it is known that fairly bulky groups such as diphenylacetylene and dmac can be successfully introduced. It seems probable that electronic factors are a major source of the observed ethene specificity, particularly when the studies[97] on the

complexes $Rh(acac)(C_2H_4)(L)$ (L = ethene and various substituted ethenes) are taken into account. These studies showed that increasing substitution of hydrogen by methyl groups reduces the stability of alkene complexes of rhodium (I). Similar results have been obtained with silver[99, 100(a), 101] and copper (I)[100] compounds. It was also found that the rhodium (I) vinyl chloride and vinyl fluoride complexes are less stable than $Rh(acac)(C_2H_4)_2$, although the trifluoroethene complex is much more stable. The workers concerned concluded that the electronic effect acts principally through the π component of the metal-alkene bond and that electropositive groups on the alkene weaken this bond while electronegative groups, present in sufficient number, strengthen it.

A dramatic demonstration of the specificity of the vacant site in $[Ru_2Cl_3(PEt_2Ph)_5]^+$ is provided by the reaction of $Ru_2Cl_4(PEt_2Ph)_5$ with $TlBF_4$ in CH_2Cl_2 under an atmosphere of commercial grade propene. The product isolated from this reaction was found to be the ethene complex (22). This unexpected product does not arise from conversion of propene to ethene but is the result of preferential coordination of the traces of ethene which contaminate this particular grade of propene.

2.3.2.1.9. The reaction with PEt_2Ph

The product from the reaction of $Ru_2Cl_4(PEt_2Ph)_5$ with equimolar quantities of $TlBF_4$ and PEt_2Ph in CH_2Cl_2 under

argon is the known cationic species $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$. Although this result is not in itself of any great value (the same species is easily prepared by other routes) it does suggest that cationic complexes of the general type $[Ru_2Cl_3(L)(PEt_2Ph)_5]^+$ where L = tertiary phosphine, phosphinite, phosphonite or phosphite may be readily prepared by this route. Such species with mixed phosphorus donor ligands have not been available previously. The reactions with bidentate ligands such as 1,2-bis(diphenylphosphino)ethane would also be of interest, offering the possibility of synthesising species with two binuclear units bridged by a $Ph_2P(CH_2)_2PPh_2$ ligand. Reactions of this type however, are outwith the scope of this thesis.

2.3.2.1.10. The reaction under argon

As has been briefly mentioned previously, when $Ru_2Cl_4(PEt_2Ph)_5$ is stirred with an equimolar amount of $TlBF_4$ in CH_2Cl_2 under argon (i.e. in the absence of any suitable replacement ligand) the products are the neutral polymeric species $[RuCl_2(PEt_2Ph)_2]_n$ (28) and the known cation $[Ru_2Cl_3(PEt_2Ph)_6]^+$.

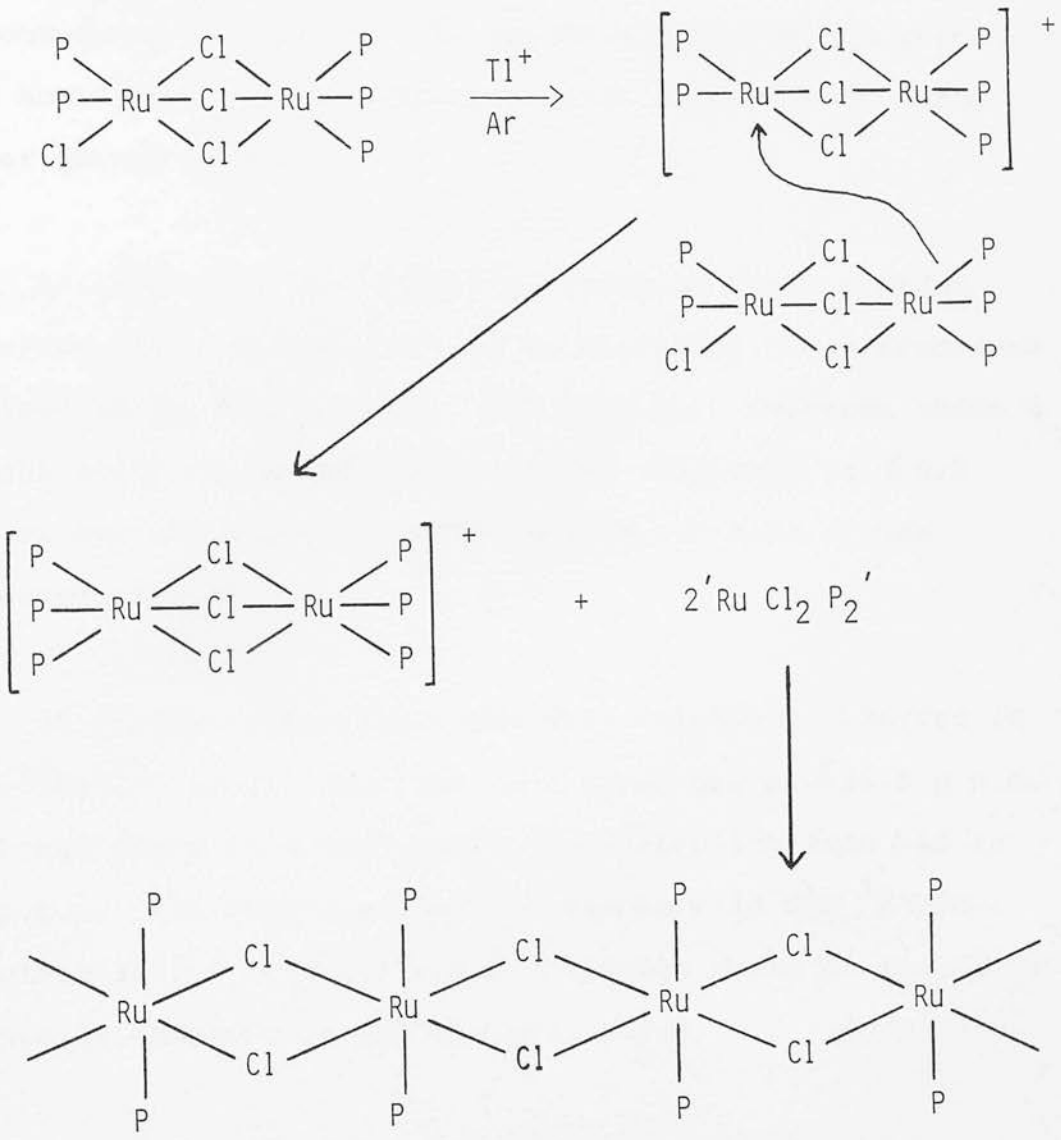
The species $[RuCl_2(PEt_2Ph)_2]_n$ has been isolated as a red solid. A band attributed to bridging ν_{Ru-Cl} is located at $308cm^{-1}$ in the i.r. spectrum. The polymeric nature of this species renders it poorly soluble in solvents such as CH_2Cl_2, $CHCl_3$ etc., and these dilute

solutions are non-conducting. The $^{31}P-[^{1}H]$ n.m.r. spectrum in $CDCl_3$ consists of a temperature-invariant singlet at δ 44.0 p.p.m.

The mechanism of formation of (28) and the hexakis phosphine binuclear cation probably involves the initial formation of a small quantity of the highly reactive coordinatively unsaturated cation $[Ru_2Cl_3(PEt_2Ph)_5]^+$, which, since no available replacement ligand is present, takes part in a "scavenging" process, gaining a PEt_2Ph group from unreacted $Ru_2Cl_4(PEt_2Ph)_5$ to give $[Ru_2Cl_3(PEt_2Ph)_6]^+$. The residual species "$Ru_2Cl_4(PEt_2Ph)_4$" rapidly rearranges and oligomerises to give (28), thus regaining the coordination number of six normally exhibited by ruthenium (II). (Scheme 2.3).

Carrying out this experiment in an n.m.r. tube in CD_2Cl_2 at 183K and monitoring the ^{1}H and $^{31}P-[^{1}H]$ n.m.r. spectra as the solution is slowly warmed up has provided some interesting information. At 183K the ^{1}H and $^{31}P-[^{1}H]$ n.m.r. spectra are essentially those of $Ru_2Cl_4(PEt_2Ph)_5$, slightly broadened by viscosity effects at this low temperature, indicating that little or no reaction has occurred. After the temperature has risen slowly to 218K the $^{31}P-[^{1}H]$ n.m.r. spectrum shows a broad resonance at δ 45.0 p.p.m. and a broad resonance at δ 35.7 p.p.m. The corresponding ^{1}H n.m.r. spectrum shows, in addition to the expected resonances (phenyl and ethyl groups), a broad resonance at δ 6.1 p.p.m. The integral of this resonance

Scheme 2.3. Chloride abstraction from $Ru_2Cl_4(PEt_2Ph)_5$ under argon



Poorly soluble in $CDCl_3$

P = PEt_2Ph

is roughly one quarter of that for the phenyl resonances in the region δ 6.9 to 7.5 p.p.m. and must be added to the phenyl resonance integrals if the phenyl to ethyl integral ratio of 1:2 is to be maintained. This suggests that the resonance at δ 6.1 p.p.m. is due to a phenyl group which for some reason is magnetically quite different from the other phenyl groups.

At 265K the $^{31}P-[^{1}H]$ n.m.r. spectrum shows a broad resonance at δ 35.5 p.p.m. and an extremely broad resonance centred at ca δ 45.0 p.p.m. The ^{1}H n.m.r. spectrum shows a slight shift of the anomalous phenyl resonance to δ 6.2 p.p.m. but the integral ratio remains the same as was observed at 218K.

At ambient temperature the only resonance observed in the $^{31}P-[^{1}H]$ n.m.r. spectrum is a broad one at δ 35.5 p.p.m. although there is a very broad hump extending from δ 40 to 47 p.p.m. The anomalous phenyl resonance in the ^{1}H n.m.r. spectrum shifts to δ 6.5 p.p.m. although again no immediate change is observed in the integral ratio.

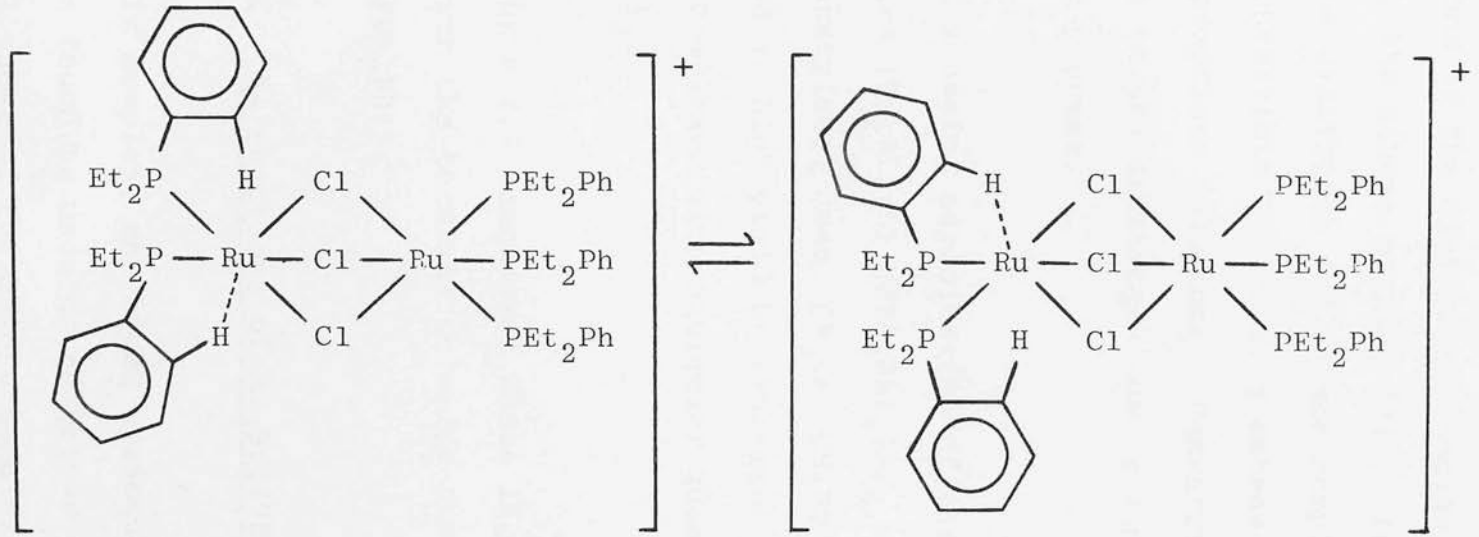
After several hours at ambient temperature the $^{31}P-[^{1}H]$ n.m.r. spectrum consists of a sharp resonance at 35.4 p.p.m., shown to be the cation $[Ru_2Cl_3(PEt_2Ph)_6]^+$ by dosing the solution with a genuine sample of this species, and a sharp resonance at δ 44.3 p.p.m. with a smaller signal at δ 43.8 p.p.m. The ^{1}H n.m.r. spectrum shows the loss of the anomalous phenyl resonance, with the integral

ratio of the phenyl resonances in the region δ 6.9 to 7.5 p.p.m. to the ethyl group resonances being 1:2 as expected for "normal" PEt_2Ph groups.

A rationalisation of these observations involves the formation of the coordinatively unsaturated cation $[Ru_2Cl_3(PEt_2Ph)_5]^+$ quantitatively from $Ru_2Cl_4(PEt_2Ph)_5$ at low temperature. At ambient temperature in contrast, the reactive cation immediately takes part in a "scavenging" reaction. At low temperatures it would seem that the vacant site in this cation is "blocked" by a phenyl ring of an adjacent PEt_2Ph group, giving rise to the anomalous resonance observed in the ^1H n.m.r. spectrum. The nature of this interaction is unknown but may involve an "agostic" phenyl proton. It is envisaged that this species is fluxional even at low temperatures, with the coordinatively unsaturated ruthenium (II) centre interacting alternately with the phenyl groups of both the nearby PEt_2Ph ligands as shown in Figure 2.8. Thus even at 180K the "$(Et_2Ph)_2Ru$" end of this species is observed as a broad resonance in the $^{31}P-[^1H]$ n.m.r. spectrum (caδ45 p.p.m.) as is the adjacent "$Ru(PEt_2Ph)_3$" end (caδ35.5 p.p.m.).

Circumstantial confirmation of the retention of the triple-chloride-bridges in this reaction is provided by bubbling ethene or N_2 through solutions thought to contain the species $[Ru_2Cl_3(PEt_2Ph)_5]^+$ (prepared and maintained at low temperature), rapidly giving the ethene and dinitrogen cationic complexes (22) and (21) respectively.

Figure 2.8 Proposed fluxional behaviour of $[Ru_2Cl_3(PEt_2Ph)_5]^+$ in $CDCl_3$



2.3.2.1.11. Ligand (L) exchange of $[Ru_2Cl_3(L)(PEt_2Ph)_5]BF_4$ (L = C_2H_4, N_2 etc.)

As mentioned previously, the vinyl chloride complex (27) can be prepared by bubbling vinyl chloride through solutions of the dinitrogen complex (21) or, to a lesser extent, the ethene complex (22). It has also been found that the dinitrogen and ethene complexes are interconvertible by bubbling ethene or dinitrogen through the appropriate solutions. Conversion of the ethene complex to the dinitrogen one is somewhat slower than the reverse process.

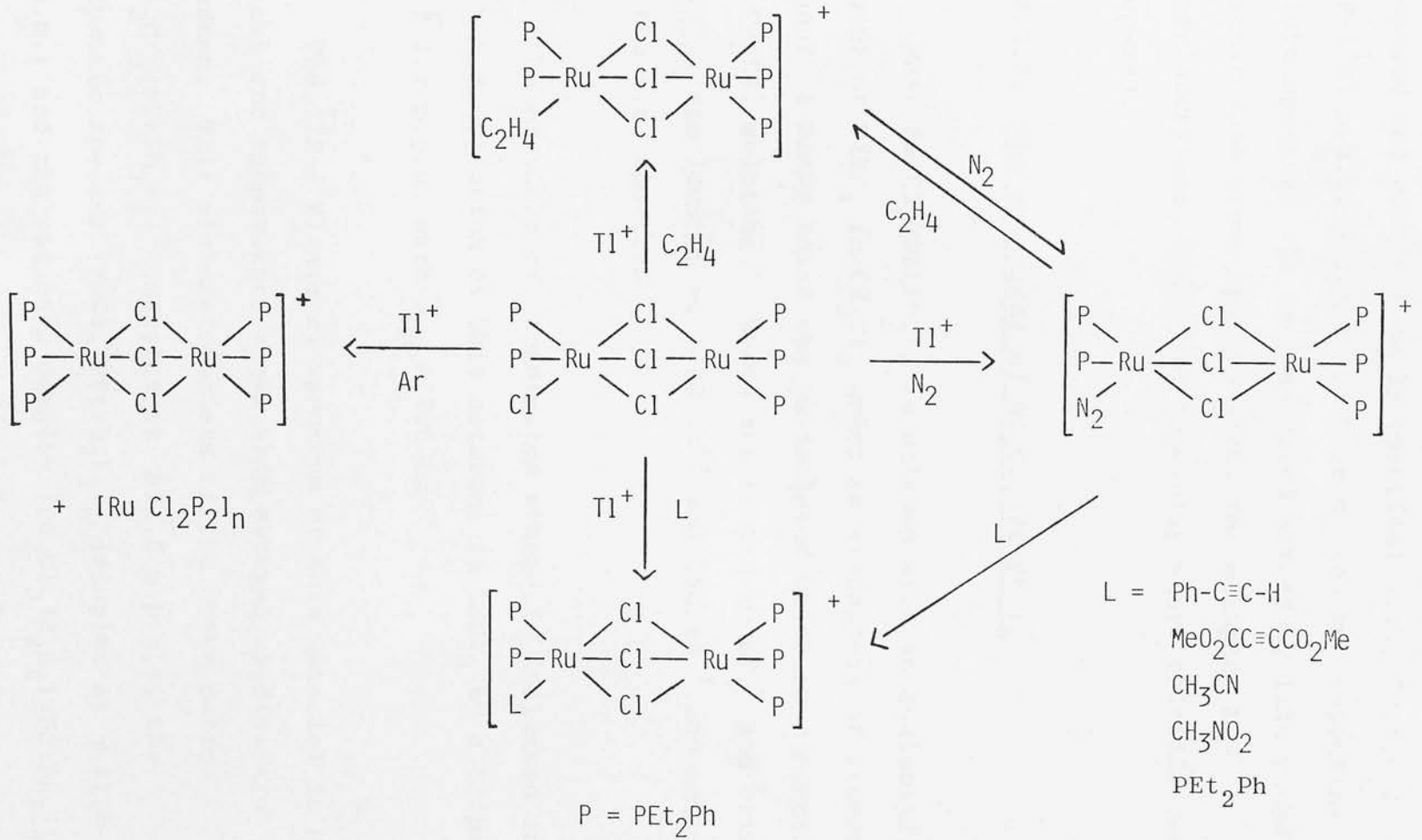
As a useful exploitation of this lability the cationic complexes $[Ru_2Cl_3(L)(PEt_2Ph)_5]BF_4$ where L = phenylacetylene, dmac, CH_3CN, CH_3NO_2 or PEt_2Ph can be prepared in high yield by treatment of the dinitrogen or ethene complexes with equimolar quantities of the ligand L in CH_2Cl_2.

Scheme 2.4 summarises these ligand exchange reactions along with the terminal chloride abstraction reactions of $Ru_2Cl_4(PEt_2Ph)_5$.

2.3.2.2. The reactions of $Ru_2Br_4(PEt_2Ph)_5$.

This complex, the bromo analogue of $Ru_2Cl_4(PEt_2Ph)_5$, has been found to undergo reactions with $TlBF_4$ which parallel those of the chloro complex. The cationic

Scheme 2.4. Summary of chloride abstraction and related reactions of $Ru_2Cl_4(PEt_2Ph)_5$



complexes $[Ru_2Br_3(L)(PEt_2Ph)_5]BF_4$ (L = N_2, C_2H_4) have been prepared and give virtually identical i.r., ^1H n.m.r. and $^{31}P-[^1H]$ n.m.r. spectra to those of the corresponding chloro species. It is considered extremely likely that further such bromo species with, for example, L = phenylacetylene, CH_3CN and hopefully vinyl chloride can be prepared.

2.3.2.3. The reactions of $Ru_2Cl_4(PEtPh_2)_5$

When $Ru_2Cl_4(PEtPh_3)_5$ is stirred with an equimolar amount of $TlBF_4$ in CH_2Cl_2 under an atmosphere of ethene for 3 hours a brown solid can be isolated which is conducting in CH_2Cl_2 solution. Bands attributed to BF_4^- and bridging ν_{Ru-Cl} are located at 1040 cm^{-1} and 260 cm^{-1} respectively in the i.r. spectrum.

The presence of coordinated ethene is indicated in the ^1H n.m.r. spectrum of this material in $CDCl_3$ by a triplet at δ 3.2 p.p.m. with J_{PH} = 2.0 Hz.

The $^{31}P-[^1H]$ n.m.r. spectrum of this material in $CDCl_3$ at ambient temperature shows that several species are present. This mixture consists of the known cation $[Ru_2Cl_3(PEtPh_2)_6]^+$ (singlet at δ 33.0 p.p.m.), the polymeric species $[RuCl_2(PEtPh_2)_2]_n$ (singlet at δ 47.8 p.p.m.) and the cationic complex $[Ru_2Cl_3(C_2H_4)(PEtPh_2)_5]BF_4$ (singlet at δ 36.0 p.p.m. and poorly resolved AB_2 pattern at

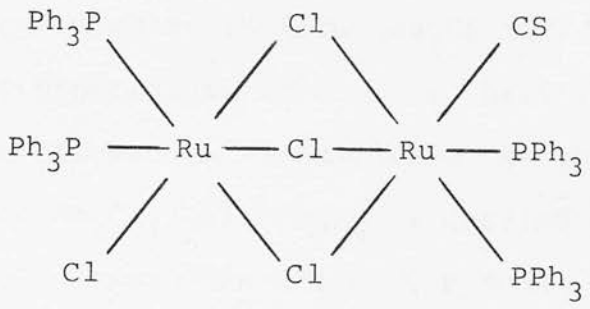
δ 37.8 p.p.m.). The ^{31}P n.m.r. resonances of the latter two species have been assigned by comparison with the resonances for the fully characterised PEt_2Ph analogues. The AB_2 pattern of the $PEtPh_2$-ethene species remains broad even on cooling to 223K. Attempts to separate this complex from the mixture have been unsuccessful.

A similar reaction under N_2 gives a reddish brown product. The i.r. spectrum of this solid shows no $\nu_{N\equiv N}$ band.

The $^{31}P-[^1H]$ n.m.r. spectrum of this material consists only of resonances for the species $[RuCl_2(PEtPh_2)_2]_n$ and $[Ru_2Cl_3(PEtPh_2)_6]^+$.

From these observations it can be concluded that the coordinatively unsaturated cation $[Ru_2Cl_3(PEtPh_2)_5]^+$ is able to coordinate ethene to a certain extent, certainly less efficiently than the PEt_2Ph analogue, and dinitrogen not at all. This is probably due to the lower basicity of the $PEtPh_2$ groups which results in less available electron density at the ruthenium (II) centre for back-donation to π-acceptor ligands such as ethene or dinitrogen.

2.3.2.4. The reactions of $Ru_2Cl_4(CS)(PPh_3)_4$



(29)

Reaction of $Ru_2Cl_4(CS)(PPh_3)_4$ (29) with an equimolar amount of $TlBF_4$ in CH_2Cl_2 in the presence of N_2, ethene or phenylacetylene gives the same orange solid which conducts in CH_2Cl_2. No evidence has been observed for coordination of any of these (potential) ligands.

This orange solid has been tentatively formulated as the coordinatively unsaturated cationic complex $[Ru_2Cl_3(CS)(PPh_3)_4]BF_4$ (30). It is then analogous to $[Ru_2Cl_3(PEt_2Ph)_5]BF_4$ (Section 2.3.2.1.10) but differs in that it is reasonably stable in solution at ambient temperature. A broad resonance at δ47.1 p.p.m. in the $^{31}P-[^1H]$ n.m.r. spectrum ($CDCl_3$) of this species is thus assigned to the fluxional PPh_3 groups at the coordinatively unsaturated end of the binuclear unit, and a sharp resonance at δ38.2 p.p.m. to the remote magnetically equivalent PPh_3 ligands. The chemical shifts of these resonances are very close to those of the corresponding AB patterns in the $^{31}P-[^1H]$ n.m.r. spectrum of the starting material.

The stability of (30) is attributed to the inability of this ligand-deficient species to take part in a "scavenging" process to form $[Ru_2Cl_3(CS)(PPh_3)_5]^+$, due to the steric constraints involved in having three PPh_3 groups in a fac arrangement. Indeed when the chloride abstraction reaction of $Ru_2Cl_4(CS)(PPh_3)_4$ is carried out in the presence of excess PPh_3 the only product isolated is the same orange cation (30).

The ^1H n.m.r. spectrum of (30) in $CDCl_3$ at ambient temperature shows no anomalous phenyl resonance of the type observed for $[Ru_2Cl_3(PEt_2Ph)_5]BF_4$ suggesting that there is no interaction between the metal centre and the phenyl rings of the PPh_3 groups via the postulated vacant site.

Support for the formulation (30) is provided by the reaction of the orange solid with chloride ion. Thus when $Ph_3(PhCH_2)PCl$ is added to a solution of (30) in $CDCl_3$ the $^{31}P-[^1H]$ n.m.r. spectrum shows the rapid growth of the two AB patterns centred at δ 36.0 and 48.0 p.p.m. associated with the starting material, $Ru_2Cl_4(CS)(PPh_3)_4$.

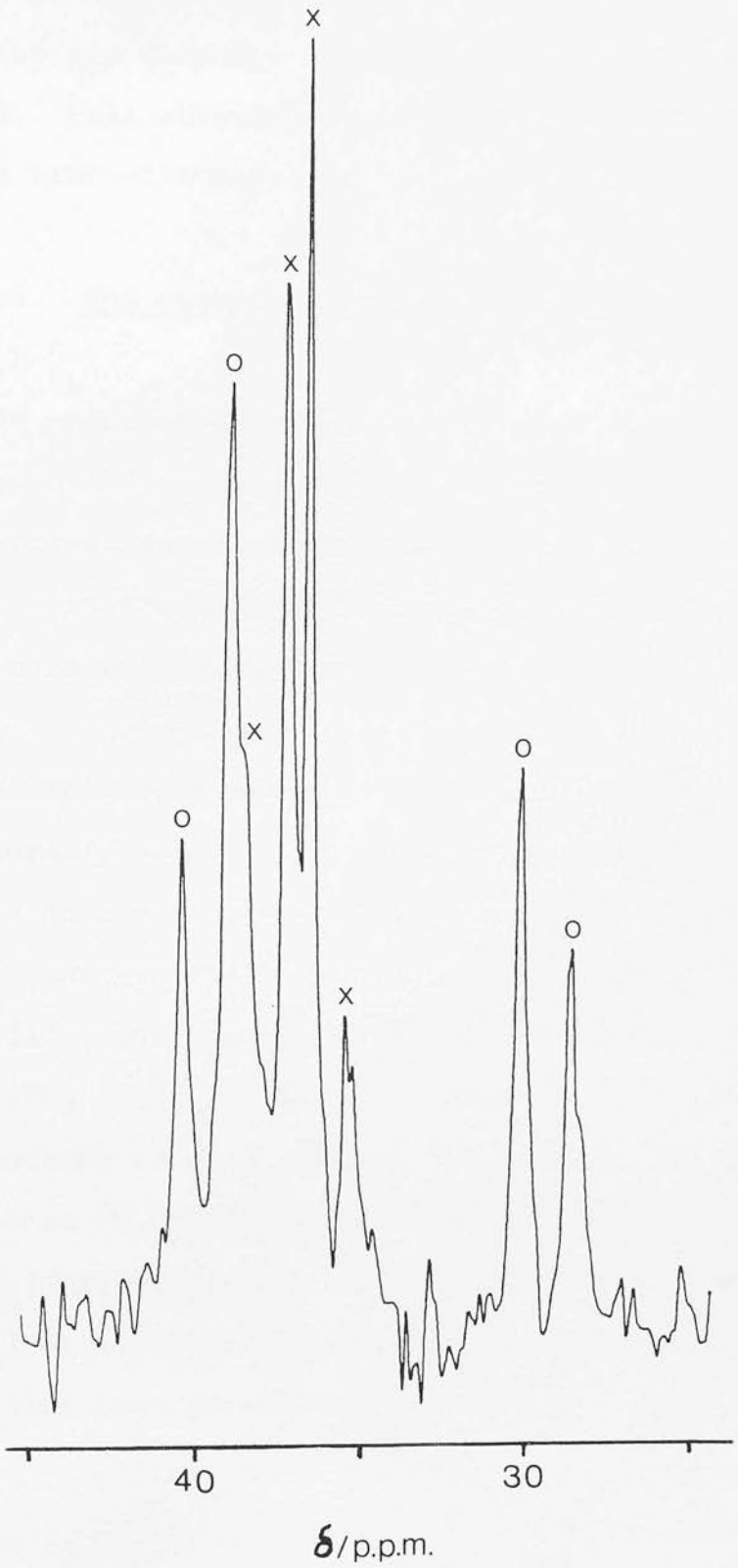
The inability of the cation (30) to coordinate ethene or dinitrogen is attributed to the low electron density at the metal centre due to the lesser basicity of the PPh_3 groups compared to PEt_2Ph or $PEtPh_2$. Steric factors are not considered to be of great importance since the cationic complex $[Ru_2Cl_3(dmso)(CS)(PPh_3)_4]BF_4$ (31) has been prepared separately by the reaction of $Ru_2Cl_4(CS)(PPh_3)_4$ with $TlBF_4$

and an equimolar amount of dmso in CH_2Cl_2. Analysis figures and the i.r. spectrum are consistent with the proposed formulation.

The $^{31}P-[^1H]$ n.m.r. spectrum of the orange species (31) at ambient temperature in $CDCl_3$ consists of two superimposed AB patterns (Figure 2.9). The AB pattern centred at δ 35.8 p.p.m. ($\Delta\nu_{AB}$ = 28 Hz; $^2J_{AB}$ = 32 Hz) is almost certainly due to the "$Ru(CS)(PPh_3)_2$" end of the initial molecule ($\Delta\nu_{AB}$ = 94 Hz; $^2J_{AB}$ = 37 Hz).

In order to ascertain whether the dmso ligand in this cation is sulphur- or oxygen-bound, the ^1H and ^{13}C n.m.r. spectra were examined. In general sulphur-bound dmso ligands give methyl group resonances in the region δ 3.2 to 3.5 p.p.m. in the ^1H n.m.r. spectrum, and to the high frequency side of free dmso (ca δ 41 p.p.m.) in the ^{13}C n.m.r. spectrum. When dmso is oxygen-bound the methyl group resonance is normally in the range δ 2.7 to 3.1 p.p.m. in the ^1H n.m.r. spectrum, and to the low frequency side of free dmso in the ^{13}C n.m.r. spectrum. It has been shown that the ^{13}C n.m.r. criterion is generally more clear-cut and reliable.[73] The ^1H n.m.r. spectrum of the cation (31) shows a resonance at δ 2.8 p.p.m. suggesting oxygen-bound dmso, whereas the ^{13}C n.m.r. spectrum shows a peak at δ 50.2 p.p.m. which is firmly indicative of sulphur-bound dmso. Thus, in the cation (31) the dmso ligand is most probably sulphur-bound, and it would be valuable to resolve the dispute between the ^1H and ^{13}C

Figure 2.9 $^{31}P-[^{1}H]$ n.m.r. spectrum of $[Ru_2Cl_3(dmso)(CS)(PPh_3)_4]BF_4$ in $CDCl_3$



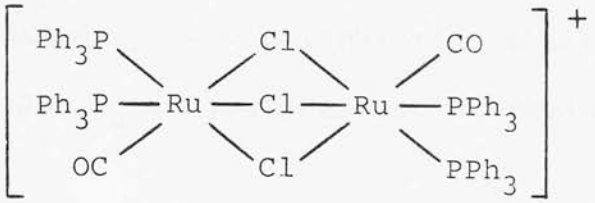
n.m.r. data.

Preliminary studies strongly suggest that the cationic complexes $[Ru_2Cl_3(L)(CS)(PPh_3)_4]\ BF_4$ with L = CH_3CN, pyridine and dimethyl sulphide can also be prepared by this method. Full characterisation of these species is underway at the time of writing.

2.3.2.5. The reactions of $Ru_2Cl_4(CO)(PPh_3)_4$

As expected from the observations made with the CS analogue, the complex $Ru_2Cl_4(CO)(PPh_3)_4$ shows no evidence of coordinating ethene or dinitrogen after terminal chloride abstraction with $TlBF_4$ in CH_2Cl_2 under an atmosphere of the appropriate gas.

Unexpectedly however, $Ru_2Cl_4(CO)(PPh_3)_4$ does differ considerably from its CS analogue in that the carbonyl complex does not appear to give a stable coordinatively unsaturated binuclear species after chloride abstraction. The solid isolated from the reaction of $Ru_2Cl_4(CO)(PPh_3)_4$ with $TlBF_4$ in CH_2Cl_2 has been shown by $^{31}P-[^1H]$ n.m.r. spectroscopy to be a mixture of species, the main components of which are the cationic dicarbonyl species $[Ru_2Cl_3(CO)_2(PPh_3)_4]^+$ (32) and one of the isomers of $Ru_2Cl_4(CO)_2(PPh_3)_3$ (see Chapter 1, Section 1.4.1), both of which have been prepared previously.



(32)

In addition, various other resonances are observed in the $^{31}P-[^{1}H]$ n.m.r. spectrum which are probably due to monomeric species.

It would seem that terminal chloride abstraction from $Ru_2Cl_4(CO)(PPh_3)_4$ results in almost immediate bridge cleavage to give monomeric species which then undergo coupling reactions to give the triple-halide-bridged species mentioned above. The anticipated coordinatively unsaturated cation $[Ru_2Cl_3(CO)(PPh_3)_4]^+$ has not been observed even when the reaction of $Ru_2Cl_4(CO)(PPh_3)_4$ with $TlBF_4$ is carried out in CD_2Cl_2 at 207K in a sealed n.m.r. tube.

The marked difference in the stabilities of $[Ru_2Cl_3(CS)(PPh_3)_4]^+$ and $[Ru_2Cl_3(CO)(PPh_3)_4]^+$ is almost certainly due to electronic factors involving the CS and CO ligands, although at the time of writing these factors are not fully understood.

Although the cation $[Ru_2Cl_3(CO)(PPh_3)_4]^+$ is unstable, preliminary studies strongly suggest that the species $[Ru_2Cl_3(L)(CO)(PPh_3)_4]^+$ where L = dmso, CH_3CN and pyridine

can be prepared by terminal chloride abstraction from $Ru_2Cl_4(CO)(PPh_3)_4$ in the presence of these particular L.

2.3.2.6. The reactions of $Ru_2Cl_4(PClPh_2)_5$

When the complex $Ru_2Cl_4(PClPh_2)_5$ is stirred with an equimolar amount of $TlBF_4$ in CH_2Cl_2 for 3 hours at ambient temperature, with or without a potential replacement ligand present the yellow starting material is recovered unchanged. If the reactions are carried out under reflux for prolonged periods, unidentified mixtures of species are obtained.

The failure to abstract terminal chloride from this complex under mild conditions is attributed to the electron-withdrawing nature of the chloride substituent on the phosphine ligands, making the terminal Ru-Cl bond stronger than in the analogous PEt_2Ph, $PEtPh_2$ or PPh_3 complexes.

2.3.2.7. The reactions of $Ru_2Cl_4(PMe_2Ph)_5$

From the reactions previously described of the complexes $Ru_2Cl_4(Y)(PR_3)_4$ (Y = CS and PR_3 = PPh_3; Y = PR_3 = PEt_2Ph, $PEtPh_2$, $PClPh_2$) it seems that ease (in thermodynamic terms) of terminal chloride abstraction and coordination of ethene, dinitrogen etc. is directly related to the basicity of, and to a lesser extent, the steric bulk of the PR_3 ligands. It therefore seemed reasonable to

predict that the complex $Ru_2Cl_4(PMe_2Ph)_5$ would be an excellent candidate for extension of the somewhat limited range of ethene and dinitrogen cationic complexes already obtained, the PMe_2Ph group being of similar steric bulk and basicity to PEt_2Ph.

When $Ru_2Cl_4(PMe_2Ph)_5$ (prepared as described in Section 2.2.1) is stirred with an equimolar amount of $TlBF_4$ in CH_2Cl_2 under an atmosphere of ethene for 3 hours a light yellow-brown solid can be isolated which is conducting in CH_2Cl_2 solution. The i.r. spectrum shows the loss of the terminal ν_{Ru-Cl} band and the presence of BF_4. No $\nu_{C=C}$ band is observed.

The ^1H n.m.r. spectrum of a $CDCl_3$ solution of this solid shows a weak triplet resonance at δ 3.1 p.p.m. (J_{PH} = 2.0 Hz) attributed to coordinated ethene. The integral of this resonance is ca one tenth of that expected for the anticipated species $[Ru_2Cl_3(C_2H_4)(PMe_2Ph)_5]BF_4$.

The $^{31}P-[^1H]$ n.m.r. spectrum at ambient temperature consists of a very intense peak at δ 22.8 p.p.m. and several weak resonances in the region δ 20 to 30 p.p.m. Thus, the main product of the reaction is $[Ru_2Cl_3(PMe_2Ph)_6]^+$, which gives rise to the intense singlet. The weak signals are attributed to the desired species $[Ru_2Cl_3(C_2H_4)(PMe_2Ph)_5]^+$, formed in low yield, and fall in the expected positions. At 226K there is some

improvement in the resolution of these resonances but they are masked to a large extent by the intense $[Ru_2Cl_3(PMe_2Ph)_6]^+$ resonance. In addition to the resonances already mentioned, there is (at 226K) a weak singlet at δ 37.4 p.p.m., due to $[RuCl_2(PMe_2Ph)_2]_n$, and a poorly resolved multiplet at δ -3.0 p.p.m. of unknown origin. At ambient temperature the weak singlet shifts to δ 34.4 p.p.m. and the low frequency multiplet is broadened.

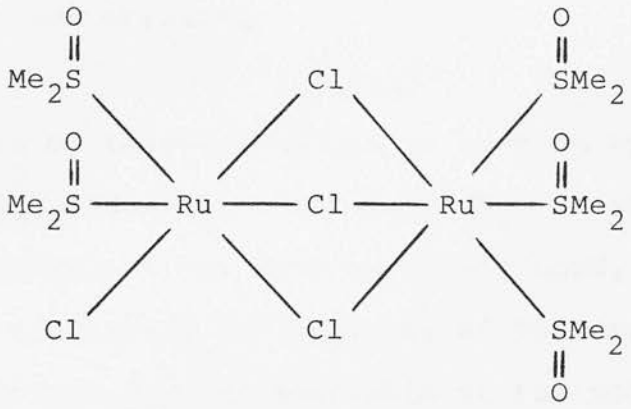
These observations suggest that on chloride abstraction from $Ru_2Cl_4(PMe_2Ph)_5$ in the presence of ethene a small amount of the cationic species $[Ru_2Cl_3(C_2H_4)(PMe_2Ph)_5]^+$ is formed but the main reaction involves "scavenging" of a PMe_2Ph group from unreacted starting material by the reactive intermediate $[Ru_2Cl_3(PMe_2Ph)_5]^+$ to give $[Ru_2Cl_3(PMe_2Ph)_6]^+$, $[RuCl_2(PMe_2Ph)_2]_n$ and another, unidentified, species. This behaviour is analogous to that of $Ru_2Cl_4(PEt_2Ph)_5$ and $TlBF_4$ in the absence of a suitable replacement ligand at ambient temperature. In the present case, the apparent preferred "scavenging" of PMe_2Ph rather than coordination of ethene is possibly due to the known high affinity of ruthenium (II) for this particular phosphine, as was mentioned in the section dealing with the preparation of $Ru_2Cl_4(PMe_2Ph)_5$.

Thus although terminal chloride abstraction from $Ru_2Cl_4(PMe_2Ph)_5$ is achieved with ease and the resulting vacant site is electronically and sterically suitable for

coordination of ethene or N_2 there is an alternative pathway for the intermediate $[Ru_2Cl_3(PMe_2Ph)_5]^+$ which is favoured under the conditions used. A similar observation has been made in the reaction of $Ru_2Cl_4(PMe_2Ph)_5$ with $TlBF_4$ under N_2. Only a very small amount of the species $[Ru_2Cl_3(N_2)(PMe_2Ph)_5]BF_4$ is obtained.

The question of thermodynamic or kinetic control of product distribution is not fully resolved.

2.3.2.8. The reactions of $Ru_2Cl_4(dmso)_5$



(33)

The complex $Ru_2Cl_4(dmso)_5$ (33) is structurally analogous to the $Ru_2Cl_4(PR_3)_5$ systems already discussed, having three chloride bridges and one terminal chloride. The five dmso ligands have been shown to be sulphur-bound by ^{13}C n.m.r. spectroscopy.[73] This compound therefore seemed a possible alternative starting material for

terminal chloride abstraction reactions in the presence of various replacement ligands to yield a new family of products.

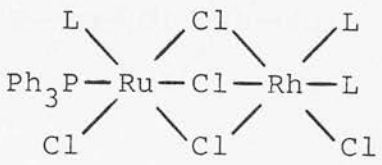
When $Ru_2Cl_4(dmso)_5$ is treated with an equimolar amount of $TlBF_4$ in CH_2Cl_2 at ambient temperature, with or without a replacement ligand present, the orange starting material is recovered unchanged after 3 hours. If the reaction is carried out under reflux TlCl is deposited and the material isolated after 3 hours has been shown by ^{13}C n.m.r. spectroscopy to contain species with both sulphur- and oxygen-bound dmso ligands. No evidence for coordination of C_2H_4 or N_2 has been obtained.

The failure of these reactions to produce species of the type $[Ru_2Cl_3(L)(dmso)_5]^+$ (L = C_2H_4, N_2) is attributed to the high strength of the terminal Ru-Cl bond, which stems from the relatively low basicity of the dmso ligands, and the low electron density available at the metal centre when this bond is ultimately cleaved under forcing conditions.

2.3.2.9. The reactions of mixed Ru(II)/Rh(III) binuclear complexes

The triple-chloride-bridged heterobimetallic complexes (34), prepared by reaction of the monomers $RuCl_2(PPh_3)_3$ and $RhCl_3L_3$ (L = PMe_2Ph, PEt_2Ph, PPr_2Ph),[83] would appear to be

excellent model systems for the type of reaction under study here.



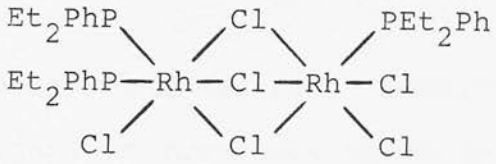
(34)

It was hoped that abstraction of terminal chloride and alkene attachment would occur exclusively at the ruthenium (II) centre.

Unfortunately, when any of the above complexes are treated with $TlBF_4$ under an atmosphere of ethene the products isolated show no indication of coordinated ethene in their ^{1}H n.m.r. spectra, although TlCl is produced during the reaction.

The $^{31}P-[^{1}H]$ n.m.r. spectra of these products are extremely complicated, indicating that terminal chloride abstraction has occurred followed by unidentified reactions to give mixtures of species.

2.3.2.10. The reactions of $Rh_2Cl_6(PEt_2Ph)_3$ (35)



(35)

This binuclear triple chloride-bridged rhodium (III) complex[88] has been treated with equimolar amounts of $TlBF_4$ in CH_2Cl_2 under atmospheres of both ethene and N_2. The product obtained in each case has been shown by $^{31}P-[^1H]$ n.m.r. spectroscopy to be a mixture of unreacted starting material and the cation $[Rh_2Cl_5(PEt_2Ph)_4]^+$ which has been previously prepared by treatment of $Rh_2Cl_6(PEt_2Ph)_3$ with $AgBF_4$ and PEt_2Ph in ethanol[88] (see Section 2.1). In the reaction with $TlBF_4$ it is probable that the intermediate cation $[Rh_2Cl_5(PEt_2Ph)_3]^+$ abstracts a PEt_2Ph group from unreacted starting material to give the tetrakis phosphine species. The fate of the starting material from which PEt_2Ph is lost is not known.

The inability of the intermediate cation to coordinate ethene or dinitrogen is not surprising since there are no known examples of rhodium(III) - alkene complexes, although a considerable number of rhodium(I) - alkene species have been prepared.

2.4. Rationalisation of observed chloride abstraction reactions

A general trend has been identified in the reactions of these binuclear complexes which is summarised in Table 2.2. This shows that terminal chloride abstraction and subsequent coordination of ethene or dinitrogen is best achieved when the tertiary phosphine groups are of relatively high basicity and have a small Tolman cone angle. In the present context the basicity of the phosphine, which determines to a large extent the strength of the terminal Ru-Cl bond and, if this is cleaved, the availability of electronic charge on the metal centre for back donation to incoming π-acceptor ligands, is considered to be of greater importance than steric factors. Thus even when the most bulky phosphine, PPh_3, is involved, fairly large ligands such as dmso or pyridine can still be introduced to the vacant site. Similarly, in the reactions of $RuCl(L)_2(\eta\text{-}C_5H_5)$ (L = various tertiary phosphines, phosphinites, phosphonites) in dmso, the rate of chloride displacement by dmso was found to be largely dependent on the donor ability of L with steric effects playing almost no role.[96]

The trend shown in Table 2.2 has also been related to another parameter exhibited by the neutral binuclear starting materials. This parameter is the electrode potential for the couple $Ru_2(II,II)/Ru_2(II,III)$, which

Table 2.2 Correlation of ease of terminal chloride abstraction and coordination of C_2H_4/N_2 in triple-chloride-bridged binuclear ruthenium (II/II) complexes with steric and electronic parameters of PR_3 ligands and the $Ru_2(II,II)/Ru_2(II,III)$ couple.

Compound	Terminal Cl^- abstraction	Coordination of C_2H_4 [a]	Coordination of N_2 [a]	Θ, deg(PR_3) [b]	ν, cm^{-1} [c]	$E_{\frac{1}{2}}$ [d] (volts) $Ru_2(II,II)/Ru_2(II,III)$
$(Et_2Ph)_2ClRuCl_3Ru(PEt_2Ph)_3$	+	+	+	136	2063.7	+ 0.47
$(Me_2Ph)_2ClRuCl_3Ru(PMe_2Ph)_3$	+	(+)	(+)	122	2065.3	+ 0.55
$(EtPh_2)_2ClRuCl_3Ru(PEtPh_2)_3$	+	(+)	-	140	2066.7	+ 0.58
$(Ph_3P)_2ClRuCl_3Ru(CO/CS)(PPh_3)_2$	+	-	-	145	2068.9	+ 0.75/0.74
$(ClPh_2P)_2ClRuCl_3Ru(PClPh_2)_3$	-	-	-		2080.7	+ 1.20
$(dmso)_2ClRuCl_3Ru(dmso)_3$	-	-	-	-	-	+ 1.40

(a) Brackets indicate incomplete reaction

(b) Tolman cone angle.[102]

(c) Frequency of the A_1 carbonyl mode of $Ni(CO)_3(PR_3)$ in CH_2Cl_2 [102]; a measure of the electronic effect of PR_3 (ν increases with decreasing basicity of PR_3).

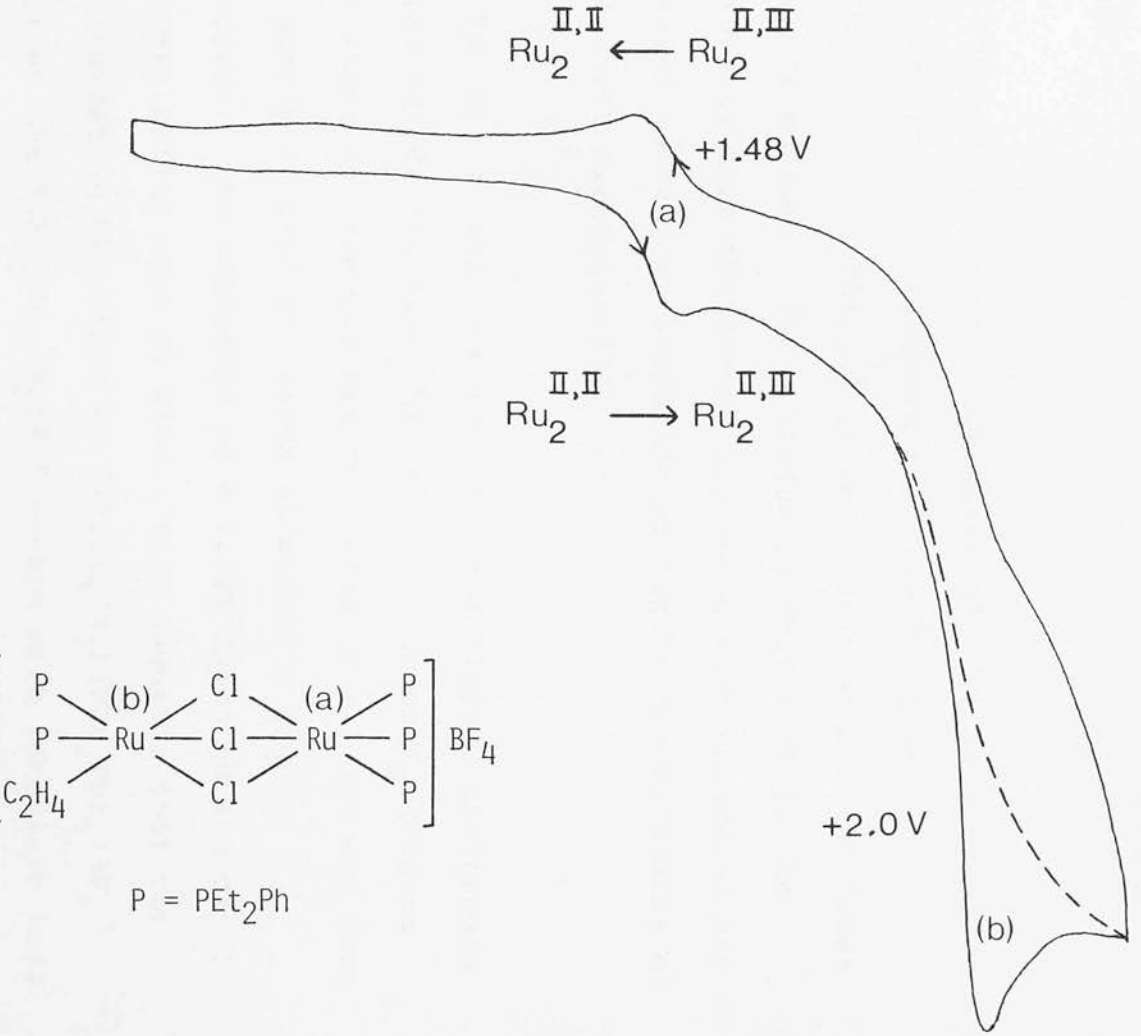
(d) Versus Ag/AgI reference at which ferrocene is oxidised at + 0.60 volts in 0.5M Bu_4NBF_4/CH_2Cl_2

occurs at the "hard" terminal chloride end of these complexes. The ease with wich the oxidation $Ru_2(II,II) \longrightarrow Ru_2(II,III)$ takes place may be taken as an approximate measure of the relative electron density at this ruthenium centre and also reflects its ability to back-donate to π-acceptor ligands once chloride abstraction has occurred. Table 2.2 shows that as this oxidation becomes more difficult terminal chloride abstraction from the neutral $Ru_2(II,II)$ complex also becomes more difficult, and that if it is achieved the ability of the coordinatively unsaturated species thus formed to bind ethene or the weaker π-acceptor dinitrogen is reduced. An added attraction of this relationship is that it allows inclusion of complexes with neutral igands other than phosphines, for example $Ru_2Cl_4(dmso)_5$ i.e. ligands for which the $\nu_{C\equiv O}$ $Ni(CO)_3L$ parameter or related index is not available.

2.5. Electrochemical studies on $[Ru_2Cl_3(L)(PEt_2Ph)_5]BF_4$ (L = C_2H_4, N_2)

The cyclic voltammogram of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22) in CH_2Cl_2 under ethene (Figure 2.10) shows a reversible one electron oxidation at +1.48V and a second irreversible oxidation at ca +2.00V. This is much like the overall pattern for the analagous species $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$ although in the latter complex the second oxidation has been found to be reversible at ambient temperature. The abundant evidence[8,11] for

Figure 2.10 The cyclic voltammogram of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ in 0.5M Bu_4NBF_4/CH_2Cl_2 vs Ag/Ag I

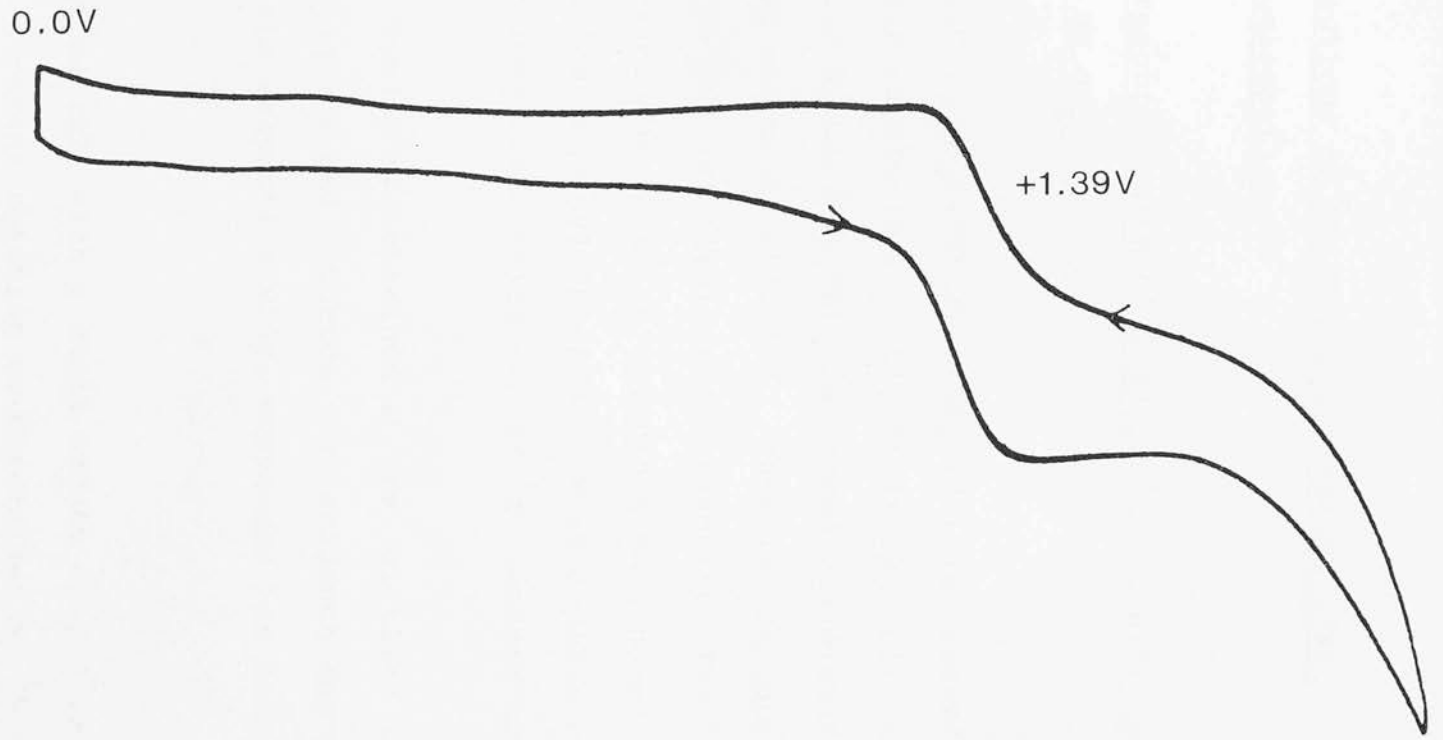


localised valencies in these binuclear species, and the reversible nature of the first wave, suggest that the initial oxidation in (22) takes place at the "$Ru(II)(PEt_2Ph)_3$" centre. The second oxidation, which remains irreversible even at 235K in the scan rate range 0.05 to 50 Vs^{-1} is attributed to the "$(Et_2PhP)_2(C_2H_4)Ru$" centre.

The electrochemical behaviour of (22) is very promising since it suggests that the dication $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]^{2+}$ is reasonably stable, at least for short periods. One stimulus to this work is the possibility that the ethene ligand in such complexes may be activated towards nucleophilic attack by the proximity of an adjacent ruthenium(III) centre.

The cyclic voltammogram of the analogous dinitrogen species $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ (21) under N_2 (Figure 2.11) shows an irreversible oxidation at + 1.39V and some very poorly defined processes at slightly higher potentials. The oxidation at + 1.39V shows no indication of reversibility even at 235K. This suggests that the first oxidation exhibited by $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ occurs at the "$(Et_2Ph)_2(N_2)Ru$" centre with immediate loss of N_2, and provides an indication of the lesser degree of back-donation of electron density from the metal to the dinitrogen ligand as compared to the situation in the ethene complex (22).

Figure 2.11 The cyclic voltammogram of $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ in 0.5M Bu_4NBF_4/CH_2Cl_2 vs Ag/Ag I



The cyclic voltammograms of the species $[Ru_2Cl_3(L)(PEt_2Ph)_5]BF_4$ where L = phenylacetylene and dmac are not as well defined as those of the ethene and dinitrogen species and require further study.

2.6. The reactions of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ with nucleophiles.

2.6.1. The reactions with Cl^-, Br^-, I^-, F^-, H_2O, OH^-, CN^-, $CH_3CO_2^-$

When $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22) is treated with a source of chloride ion (HCl, LiCl, $Ph_3(PhCH_2)PCl$), the neutral species $Ru_2Cl_4(PEt_2Ph)_5$ is formed via displacement of coordinated ethene by chloride. This is, of course, the reversal of the initial displacement reaction. The ^1H n.m.r. spectra of the reaction solutions show no evidence for the formation of vinyl chloride. This applies even when the reactions are carried out at low temperature.

Similar results are obtained in the reactions of (22) with bromide, iodide and fluoride. No evidence for the formation of the respective vinyl compounds has been observed.

Treatment of (22) with a small amount of H_2O in $CDCl_3$ results in no apparent reaction as determined by ^1H n.m.r. spectroscopy, even after several weeks. If aqueous NaOH

is added instead of H_2O, slow displacement of coordinated ethene is observed, but with no formation of ethanal. The $^{31}P-[^1H]$ n.m.r. spectrum of the reaction solution is complex, probably due to the formation of species with mixed chloride and hydroxide bridges, as has been found in the reactions of $Ru_2Cl_4(Y)(PPh_3)_4$ (Y = CO, CS) with aqueous NaOH.[73]

The $^{31}P-[^1H]$ n.m.r. spectra of the reaction solutions obtained on treating (22) in $CDCl_3$ with cyanide or acetate ions are also complex. The ^1H n.m.r. spectra show that displacement of coordinated ethene has occurred and that vinyl compounds are not formed.

To summarise, the only reaction observed when the ethene species (22) is treated with a wide variety of nucleophiles is displacement of the ethene ligand. No evidence for nucleophilic attack on the coordinated ethene has been obtained under the experimental conditions described.

2.6.2. The reaction with Cl_2

Electrochemical studies on the cationic ethene complex (22) have shown that the mixed-valence dication $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]^{2+}$ is reasonably stable (Section 2.5). It has also been shown that the sole reaction of (22) when treated with chloride ion (or other

nucleophiles) is displacement of the ethene ligand. This suggests that the coordinated ethene in (22) is not sufficiently activated towards nucleophilic attack. In view of this it seems worthwhile to explore the reactions of the Ru_2(II,III) dication $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]^{2+}$ with nucleophiles, particularly chloride ion, since the ethene ligand in this species may be more susceptible to attack. Treatment of the cation (22) with Cl_2 was considered to be a potentially clean, single-step method of generating the mixed-valence dication and chloride ion in situ.

A solution of (22) in CH_2Cl_2 was treated with a solution of Cl_2 in CCl_4 such that the molar ratio of (22) to Cl_2 was 2:1, i.e. just enough Cl_2 was added to oxidise the cation (22) to the dication and produce enough chloride ion to give an ethene to chloride ratio of 1:1. To avoid loss of volatile products the reaction was carried out in a closed vessel, consisting of a round bottomed flask sealed with a rubber septum. The flask was purged with argon prior to the addition of the CH_2Cl_2 solution of (22). The solution of Cl_2 in CCl_4 was added by means of a syringe through the rubber septum.

On addition of the Cl_2 solution (with stirring) the reaction solution changed instantly from light brown to a darker reddish-brown. Samples of both the gas phase above the reaction solution and the solution itself were

subjected to gas chromatographic analysis immediately upon addition of the Cl_2 solution, and at regular intervals thereafter. (Gas chromatography was used instead of ^1H n.m.r. spectroscopy to detect volatile products since the proposed reaction involves the formation of paramagnetic ruthenium (III) species which would result in a considerable loss of n.m.r. resolution).

The gas phase showed a gradual but steady increase in the concentration of ethene, with no indication whatsoever of the presence of vinyl chloride. The reaction solution also showed no trace of vinyl chloride at any time.

The same reaction was carried out at 233K and gave very similar results, with no vinyl chloride being detected.

On addition of n-hexane to the final solution from both the ambient and low temperature reactions, a reddish-brown solid precipitated. The ^1H n.m.r. spectrum of this material in $CDCl_3$, although somewhat poorly resolved as expected, showed no signals attributable to free or coordinated vinyl chloride, but did show the presence of a small amount of coordinated ethene. The $^{31}P-[^1H]$ n.m.r. spectrum was complex, with the signals broadened by the presence of paramagnetic ruthenium (III) species.

These observations suggest that, as with its $Ru_2(II,II)$ precursor (22), the main reaction of the mixed-valence dication in the presence of chloride ion is the displacement of the ethene ligand, with no nucleophilic attack occurring on coordinated ethene.

2.7. Conclusions

It has been found that cationic complexes of the type $[Ru_2X_3(L)(PEt_2Ph)_5]BF_4$ ($X = Cl^-, Br^-$; $L = C_2H_4, N_2$ etc.) are readily prepared under mild conditions and in almost quantitative yield when the neutral complex $Ru_2X_4(PEt_2Ph)_5$ is treated with $TlBF_4$ in the presence of L in a non-coordinating solvent.

Altering the neutral ligand L' in complexes of the general type $Ru_2Cl_4(Y)(L')_4$ ($Y = CO, CS, L' = PPh_3$; $Y = L' = PEt_2Ph, PMe_2Ph, PEtPh_2, PClPh_2$, dmso) has been shown to have a profound effect on the ease with which the terminal chloride ligand may be abstracted using $TlBF_4$ and on the ability of the coordinatively unsaturated cationic species $[Ru_2Cl_3(Y)(L')_4]^+$ to bind π-acceptor ligands such as ethene and dinitrogen. This is shown to be related to the electronic effect of L' on the ruthenium (II) centre from which the terminal chloride ligand is abstracted. Steric constraints to coordination of the ligands L are considered to be of minor importance in the systems studied.

Reaction of the cationic complex $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ with a wide variety of nucleophiles results only in displacement of the ethene ligand with no evidence for nucleophilic attack on coordinated ethene. This is attributed to the charge distribution on the complex which renders nucleophilic attack at the metal centre more favourable than nucleophilic attack on the ethene ligand. Preferential attack of chloride at the metal centre has also been observed in the mixed-valence dication $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]^{2+}$.

These observations suggest that nucleophilic attack on ethene may be more favourable when the ethene is coordinated to a neutral binuclear ruthenium (II) species. This possibility is explored in the work described in the next chapter.

2.8. Experimental Methods

Microanalyses were performed in the Chemistry Departments of the University of Edinburgh and the University of St. Andrews. Melting points (uncorrected) were determined on a Kofler hot-stage microscope and conductivity measurements with a Portland Electronics Model 310 conductivity bridge. Infrared spectra were recorded on a Perkin-Elmer 557 grating spectrometer, using Nujol mulls on CsI plates. Variable temperature ^1H and $^{31}P-[^1H]$

n.m.r. spectra were run on JEOL FX60Q and Bruker WP80, 200SY and WH360 pulsed Fourier-transform spectrometers (^{1}H n.m.r. chemical shifts are reported in p.p.m. to high frequency of $SiMe_4$, $^{31}P-[^{1}H]$ n.m.r. chemical shifts to high frequency of 85% H_3PO_4). Standard Schlenk and vacuum line techniques were used when necessary.

Electrochemical studies were performed using a PAR model 170 potentiostat and programmer with platinum working and auxiliary electrodes and Ag/Ag^{+} or Ag/AgI reference electrodes (against which ferrocene is oxidised at $E_{\frac{1}{2}}$ = +0.05 and +0.60V respectively). Non-aqueous 0.50M Bu_4NBF_4/CH_2Cl_2 or CH_3CN electrolyte solutions were used throughout.

Materials

The following were prepared using literature methods: cis-$RuCl_2(PMe_2Ph)_4$[7b], $[Ru_2Cl_3(PMe_2Ph)_6]Cl$[7b], $Ru_2Cl_4L_5$ (L = PEt_2Ph, $PEtPh_2$, $PClPh_2$[7b], dmso[103]), $Ru_2Br_4(PEt_2Ph)_5$[73], $Ru_2Cl_4(Y)(PPh_3)_4$ (Y = CO, CS)[4a,d], $[L^1LClRuCl_3RhClL_2]$ (L^1 = PPh_3, L = PEt_2Ph, PMe_2Ph, PPr_2Ph)[83], $Rh_2Cl_6(PEt_2Ph)_3$[88]. $TlBF_4$ was prepared by reaction of $Tl(CH_3CO_2)$ with HBF_4[104]. Ethene, propene (Matheson), styrene, phenylacetylene, dimethylacetylenedicarboxylate, cyclooctadiene and cyclooctatetraene (B.D.H.) were used as supplied. Vinyl chloride was provided by New Science Group of Imperial Chemical Industries p.l.c. Acetonitrile was

purified by the method of Walter and Ramaley[105] and was freshly distilled from P_2O_5 before use. Methylene chloride was allowed to stand for 1 week over KOH pellets and dried by distillation over P_2O_5. n-Hexane was dried over sodium wire.

def-Tri-μ-chloro-a-chloro-bcghi-pentakis (dimethylphenylphosphine) diruthenium(II), $Ru_2Cl_4(PMe_2Ph)_5$

A suspension of the yellow complex cis-$RuCl_2(PMe_2Ph)_4$ in benzene was irradiated at 254 nm for 3 hours under N_2. The resulting orange solution was concentrated under vacuo and on addition of n-hexane the yellow species $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ was precipitated. After filtering off this yellow solid the orange filtrate was concentrated in vacuo to give an orange precipitate of the title complex. Small amounts of $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ in the orange solids thus isolated were removed by repetition of the benzene/n-hexane separation process. Yields of $Ru_2Cl_4(PMe_2Ph)_5$ were variable and in the range 50 to 75%.

m.p. 120-124°C

Found: C, 47.2; H, 5.5. Calc. for $C_{40}H_{55}Cl_4P_5Ru_2$: C, 46.4; H, 5.3%.

Mull i.r. spectrum : ν_{Ru-Cl} 300, 245(m) cm^{-1}.

Trans-dichlorotetrakis (dimethylphenylphosphine) ruthenium(II), trans-$RuCl_2(PMe_2Ph)_4$

A suspension of the yellow complex cis-$RuCl_2(PMe_2Ph)_4$ was irradiated at 360 nm for 3 hours under N_2. The yellow solution was evaporated to dryness *in vacuo* and the yellow oil triturated with n-hexane to give a yellow powder. Yield 100%. m.p. 150-153°C.

Found : c, 53.2; H, 6.1. Calc. for $C_{32}H_{44}Cl_2P_4Ru$: C, 53.0; H, 6.1%.

Mull i.r. spectrum : ν_{Ru-Cl} 315 cm^{-1}.

Attempted pyrolysis of $[Ru_2Cl_3(PMe_2Ph)_6]Cl.nEtOH$

The yellow cationic complex $[Ru_2Cl_3(PMe_2Ph)_6]Cl.$ nEtOH (prepared by reaction of $RuCl_2(PPh_3)_3$ with PMe_2Ph in ethanol) was pyrolysed at 523K for 24 hours in an evacuated, sealed Carius tube. The resulting yellow-orange gum was triturated with n-hexane to give a pale mustard coloured powder, identified as $RuCl_2(CO)(PMe_2Ph)_3$. The yield was 100%. m.p. 165-168°C(d).

Found: C, 49.3; H, 5.5. Calc. for $C_{25}H_{33}Cl_2OP_3Ru$: C, 48.9; H, 5.4%.

Mull i.r. spectrum: $\nu_{C\equiv O}$ 1940(s), ν_{Ru-Cl} 225(m), 293(w) cm^{-1}.

def-Tri-μ-chloro-abcgh-pentakis (diethylphenylphosphine)-i-(dinitrogen) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ (21).

The orange complex $Ru_2Cl_4(PEt_2Ph)_5$ (0.50g,0.43mmol) and $TlBF_4$ (0.13g,0.45mmol) were stirred in dry degassed CH_2Cl_2 ($20cm^3$) under an atmosphere of N_2 for 3 hours. The fine precipitate of TlCl was filtered off and the solvent removed from the filtrate by continuously blowing N_2 through the bulk of the yellow-brown solution. Trituration of the brown residue with degassed n-hexane gave a mustard coloured powder which was filtered off from the n-hexane and stored under N_2. m.p. 75-80°C(d) (0.52g, 97%).
Found: C, 48.1; H, 6.4; N, 1.9. Calc. for $C_{50}H_{75}BCl_3F_4P_5N_2Ru_2$: C, 47.9; H, 6.0; N, 2.2%.
Mull i.r. spectrum: $\nu_{N\equiv N}$ 2140(S), BF_4^- 1040 (s,br), ν_{Ru-Cl} 255(w) cm^{-1}.

def-Tri-μ-chloro-abcgh-pentakis(diethylphenylphosphine)-i-(η-ethene) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22).

The same techniques were used to prepare this cationic complex as were used for the dinitrogen species (21), except that all operations were carried out under ethene and the product was stored under ethene.
m.p. 72-80°C(d) (Yield 97%)
Found: C, 50.1; H, 6.4. Calc. for $C_{52}H_{79}BCl_3F_4P_5Ru_2$: C, 49.8; H, 6.3%

Mull i.r. spectrum: BF_4^- 1030 (s,br), ν_{Ru-Cl} 240(w) cm^{-1}.

def-Tri-μ-chloro-abcgh-pentakis (diethylphenylphosphine)-i-(η-phenylacetylene) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(PhC{\equiv}CH)(PEt_2Ph)_5]BF_4$ (23).

The orange complex $Ru_2Cl_4(PEt_2Ph)_5$ (0.50g, 0.43 mmol), $TlBF_4$ (0.13g, 0.45 mmol) and phenylacetylene (0.05g, 0.49 mmol) were stirred in dry, degassed CH_2Cl_2 (20 cm^3) under argon for 3 hours. The fine precipitate of TlCl was filtered from the solution under argon and the filtrate evaporated to dryness in vacuo. The brown residue was triturated with degassed n-hexane to give a light brown powder which was stored under argon. m.p. 80-85°C(d) (0.54g, 96%).

Found: C, 53.3; H, 6.4. Calc. for $C_{58}H_{81}BCl_3F_4P_5Ru_2$: C, 52.4; H, 6.1%

Mull i.r. spectrum: $\nu_{C{\equiv}C}$ 1972(m), ν_{C-H}(alkyne)3310(w), BF_4^- 1040 (s,br), ν_{Ru-Cl} 250(w) cm^{-1}.

def-Tri-μ-chloro-abcgh-pentakis(diethylphenylphosphine)-i-(η-dimethylacetylenedicarboxylate)diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(dmac)(PEt_2Ph)_5]BF_4$ (24)

This species was prepared using the same techniques described above for the phenylacetylene species (23). m.p.80-86°C(d) (Yield 95%).

Found: C, 50.2; H, 6.2. Calc. for $C_{56}H_{81}BCl_3O_4F_4P_5Ru_2$: C, 49.1; H, 5.9%.

Mull i.r. spectrum: $\nu_{C\equiv C}$ 1880 (m), $\nu_{C=O}$ 1720 (m), 1705(sh), BF_4^- 1030(s,br), ν_{C-O} 1235(s,br), ν_{Ru-Cl} 250(w) cm^{-1}.

def-Tri-μ-chloro-a-(acetonitrile)-bcghi-pentakis (diethylphenylphosphine) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(CH_3CN)(PEt_2Ph)_5]BF_4$ (25).

This species was prepared using the same techniques described above for the phenylacetylene species (23). m.p.103-105°C(d) (Yield 92%).

Found: C, 49.8; H, 6.4; N, 1.0, Calc. for $C_{52}H_{78}BCl_3F_4P_5NRu_2$: C, 49.3; H, 6.2; N, 1.1%.

Mull i.r. spectrum: $\nu_{C\equiv N}$ 2270(w), BF_4^- 1040 (s,br), ν_{Ru-Cl} 250(w) cm^{-1}.

def-Tri-μ-chloro-abcgh-pentakis(diethylphenylphosphine)-i-(nitromethane) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(CH_3NO_2)(PEt_2Ph)_5]BF_4$ (26).

This species was prepared using the same techniques described above for the phenylacetylene species (23). m.p. 96-98°C(d) (Yield 94%).

Found : C, 47,9; H, 6.2; N,1.0. Calc. for $C_{51}H_{78}BCl_3O_2F_4P_5NRu_2$: C, 47.6; H, 6.1; N, 1.1%.

Mull i.r. spectrum: $\nu_{N=O}$ 1550, 1350(w), BF_4^- 1040(s,br), ν_{Ru-Cl} 250 cm^{-1}.

def-Tri-μ-chloro-abcgh-pentakis (Diethylphenylphosphine)-i-(η-vinyl chloride) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(CH_2{=}CHCl)(PEt_2Ph)_5]BF_4$ (27)

The cationic complex $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ (21) (0.25g, 0.20mmol) was dissolved in CH_2Cl_2 (20 cm^3) which had been saturated with vinyl chloride. A steady stream of vinyl chloride was bubbled through the solution for 30 minutes, by which time the volume of the solution had been considerably reduced. On addition of excess n-hexane (saturated with vinyl chloride) a brown oil separated from the solution. The supernatant solution was decanted from the oil, which was then triturated with a further portion of n-hexane to give a mustard coloured powder. This was stored under vinyl chloride but rapidly became sticky and turned green even when stored at low temperature. (0.24g, 93%). No analytical data were obtained for this solid. Mull i.r. spectrum: $\nu_{C=C}$ 1605(w), BF_4^- 1040 (s,br), ν_{C-Cl} 680(sh), ν_{Ru-Cl} 250(w) cm^{-1}.

Note: In addition to the methods already described for the preparation of the cationic complexes (22,23,24,25,26), they can also be prepared by treatment of the species $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ with an equimolar amount of the appropriate ligand in CH_2Cl_2.

$[RuCl_2(PEt_2Ph)_2]_n$ (28)

The orange complex $Ru_2Cl_4(PEt_2Ph)_5$ (0.50g, 0.43mmol) and $TlBF_4$ (0.13g, 0.45mmol) were stirred in degassed CH_2Cl_2 (20 cm^3) under argon for 3 hours. After filtering off the fine precipitate of TlCl the volume of the brown solution was reduced *in vacuo* and excess n-hexane added to give a yellow-brown precipitate of $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$. This solid was filtered off and the filtrate stored in a refrigerator for 12 hours. The species $[RuCl_2(PEt_2Ph)_2]_n$ was precipitated as a red solid. This solid is of limited solubility in solvents such as CH_2Cl_2 and $CHCl_3$. m.p. 120-123°C (0.17g).

Found: C, 47.3; H, 6.1. Calc. for $[C_{20}H_{30}Cl_2P_2Ru]_n$: C, 47.6; H, 6.0%.

Mull i.r. spectrum: ν_{Ru-Cl} 308(m) cm^{-1}.

def-Tri-μ-bromo-abcgh-pentakis(diethylphenylphosphine)-i-(dinitrogen) diruthenium(II) tetrafluoroborate, $[Ru_2Br_3(N_2)(PEt_2Ph)_5]BF_4$.

This cationic complex was prepared as for the chloro analogue (21). m.p. 73-80°C(d).

Found: C, 43.7; H, 5.6; N, 1.8. Calc. for $C_{50}H_{75}BBr_3F_4P_5N_2Ru_2$: C, 43.3; H,5.4; N, 2.0%.

Mull i.r. spectrum: $\nu_{N\equiv N}$ 2145(s), BF_4^- 1040(s,br), ν_{Ru-Br} 250(w) cm^{-1}.

def-Tri-μ-bromo-abcgh-pentakis (diethylphenylphosphine)-i-(η-ethene) diruthenium(II) tetrafluoroborate

$[Ru_2Br_3(C_2H_4)(PEt_2Ph)_5]BF_4$

This cationic complex was prepared as for the chloro analogue (22). m.p. 79-85°C(d).

Found: C, 45.3; H, 5.7. Calc. for $C_{52}H_{79}BBr_3F_4P_5Ru_2$: C, 45.0; H, 5.7%.

Mull i.r. spectrum: BF_4^- 1040(s,br), ν_{Ru-Br} 250(w) cm^{-1}.

def-Tri-μ-chloro-abgh-tetrakis(triphenylphosphine)-c-(thiocarbonyl) diruthenium(II) tetrafluoroborate,

$[Ru_2Cl_3(CS)(PPh_3)_4]BF_4$ (30)

The complex $Ru_2Cl_4(CS)(PPh_3)_4$ (0.10g, 0.07mmol) and $TlBF_4$ (0.02gm 0.07mmol) were stirred in degassed CH_2Cl_2 (10 cm^3) for 3 hours under N_2. The fine precipitate of TlCl was filtered off under N_2 and the volume of the filtrate reduced *in vacuo*. On addition of degassed n-hexane an orange solid precipitated and was filtered off. This solid was found to be contaminated with small amount of $OPPh_3$ on each occasion the reaction was carried out, despite the rigorous exclusion of air. For this reason analytical figures were variable. A typical yield was 0.07g, 67%.

Mull i.r. spectrum: $\nu_{C\equiv S}$ 1288(s), BF_4^- 1040(s,br), ν_{Ru-Cl} 230(w) cm^{-1}.

def-Tri-μ-chloro-a-(dimethylsulphoxide)-bcgh-tetrakis (Triphenylphosphine)-i-(thiocarbonyl) diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(dmso)(CS)(PPh_3)_4]BF_4$ (31).

The reaction procedure for this species was identical to that for (30) above except for the addition of dmso (4.0 μl). The cationic complex was isolated as an orange solid. m.p. 136-137°C. (0.07g, 64%).

Found: C, 57.6; H, 4,4. Calc. for $C_{75}H_{66}BCl_3F_4P_4S_2ORu_2$: C, 57.4; H, 4.2%.

Mull i.r. spectrum: $\nu_{C\equiv S}$ 1290(S), BF_4^- 1050(s,br), ν_{Ru-Cl} 250(w) cm^{-1}.

CHAPTER 3

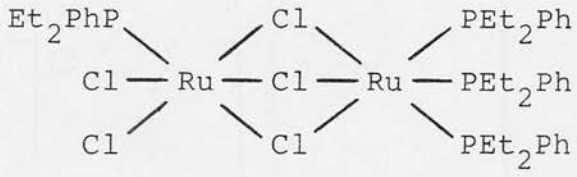
REDUCTION OF $Ru_2Cl_5(PEt_2Ph)_4$

IN THE PRESENCE OF ALKENES AND ALKYNES

CHAPTER 3. REDUCTION OF $Ru_2Cl_5(PEt_2Ph)_4$ IN THE PRESENCE OF ALKENES AND ALKYNES.

3.1. INTRODUCTION

The "asymmetric" (with respect to the positions of the terminal chloride ligands) mixed-valence complex $Ru_2Cl_5(PEt_2Ph)_4$ (36) undergoes a reversible one-electron oxidation at +1.27V and a reversible one-electron reduction at -0.28V (versus Ag/AgI at which ferrocene is oxidised at +0.60V) as shown in Figure 3.1.[8]

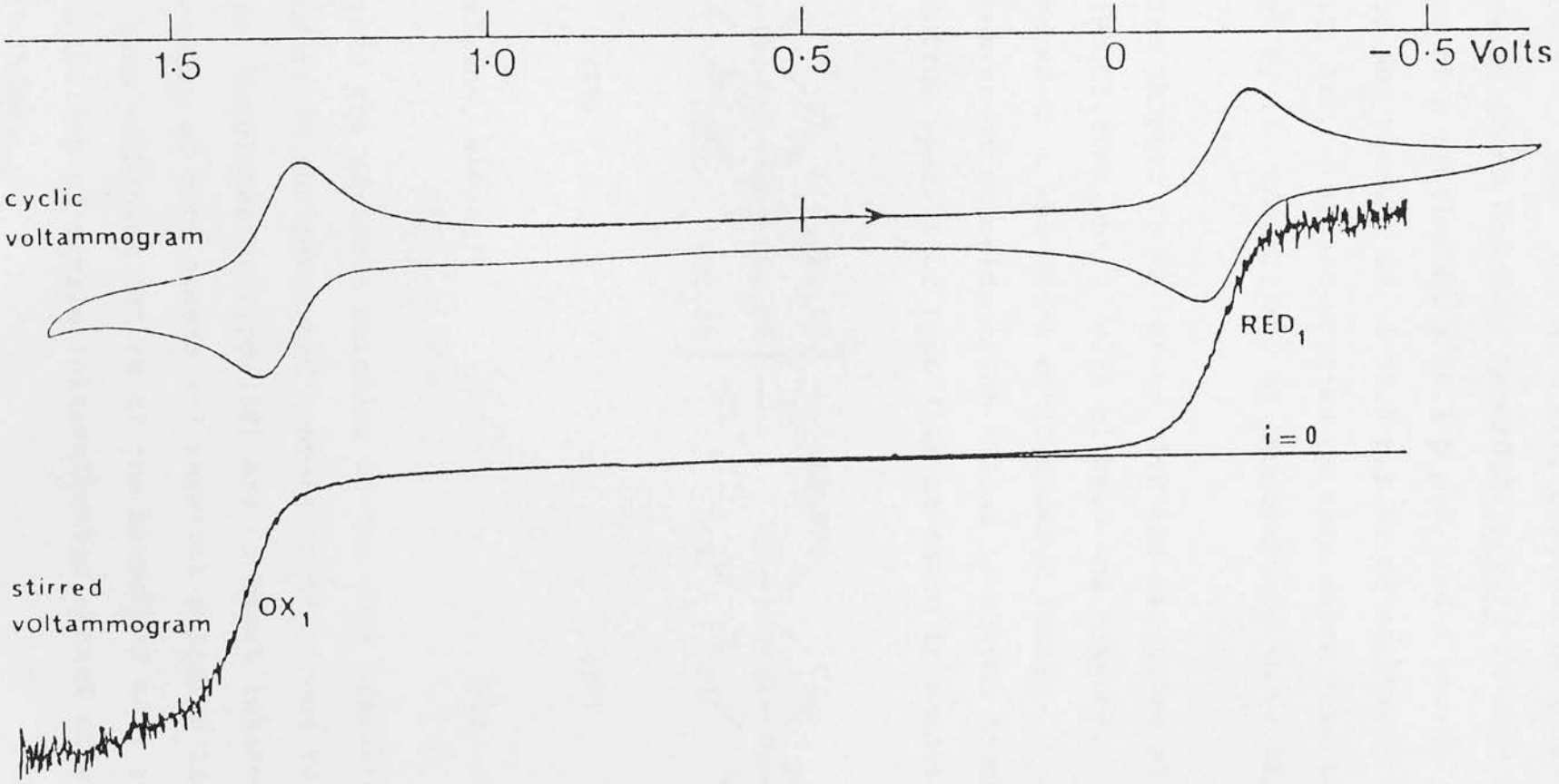


(36)

This electrochemical behaviour is typical of "asymmetric" mixed-valence complexes of type (36) i.e. they all undergo facile reduction at the "hard" (terminal chloride) site of the binuclear unit and difficult oxidation at the adjacent "soft" metal centre, with a separation of the redox steps of ca 1.5V.

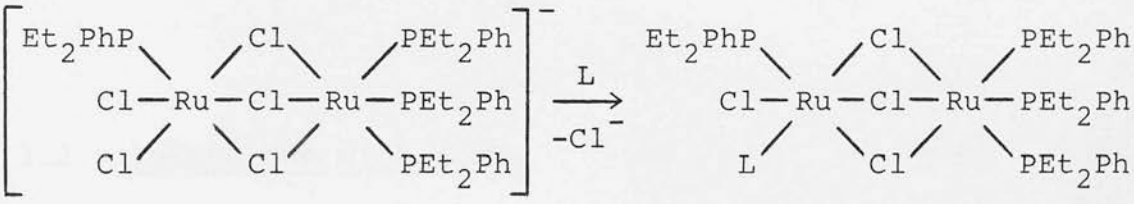
The yellow-orange Ru_2 (II,II) anion $[Ru_2Cl_5(PEt_2Ph)_4]^-$ (37) can be electrogenerated at 213K in Bu_4NBF_4/CH_2Cl_2

Figure 3.1. Stirred and unstirred voltammograms of $Ru_2Cl_5(PEt_2Ph)_4$



solution.[106] The $^{31}P-[^{1}H]$ n.m.r. spectrum of this diamagnetic anion has been recorded in situ at 213K and consists of a singlet at δ 56.2 p.p.m. and a poorly resolved AB_2 pattern at δ 33.8 p.p.m. of relative intensity 1:3. Further studies on this anion have been hindered by its instability at temperatures above 213K.

This chapter is concerned with the reactions of the anion $[Ru_2Cl_5(PEt_2Ph)_4]^-$ with alkenes and alkynes. It was anticipated that the anion would undergo facile displacement of chloride by an alkene or alkyne ligand to give neutral species of type (38) as shown in equation 3.1.



(37) (38)

(L = alkene, alkyne) ... 3.1

Since the ultimate stimulus of the work presented in this thesis is the catalysed conversion of ethene to vinyl chloride, complexes of type (38) are of great interest. The presence of both alkene and terminal chloride ligands on the same ruthenium centre of the binuclear unit permits the possibility of facile intramolecular attack of chloride on the alkene.

Until this work the anion (37) had been generated only electrochemically at 213K. Unfortunately the solution thus obtained also contains large quantities of the supporting electrolyte (Bu_4NBF_4), making isolation of the product in a reasonably pure state extremely difficult and unsuitable for further study. For this reason it was decided to investigate chemical reduction of the mixed-valence complex (36) using reducing agents such as zinc amalgam, magnesium turnings and $NaBH_4$. An added attraction of these chemical reducing agents is that the Na^+ ion of $NaBH_4$ and the oxidised forms of the zinc amalgam and magnesium, Zn^{2+} and Mg^{2+} respectively, may also act as chloride-abstracting agents, facilitating the desired reaction of the anion (37).

3.2. Reductions with $NaBH_4$

3.2.1. The reaction with phenylacetylene

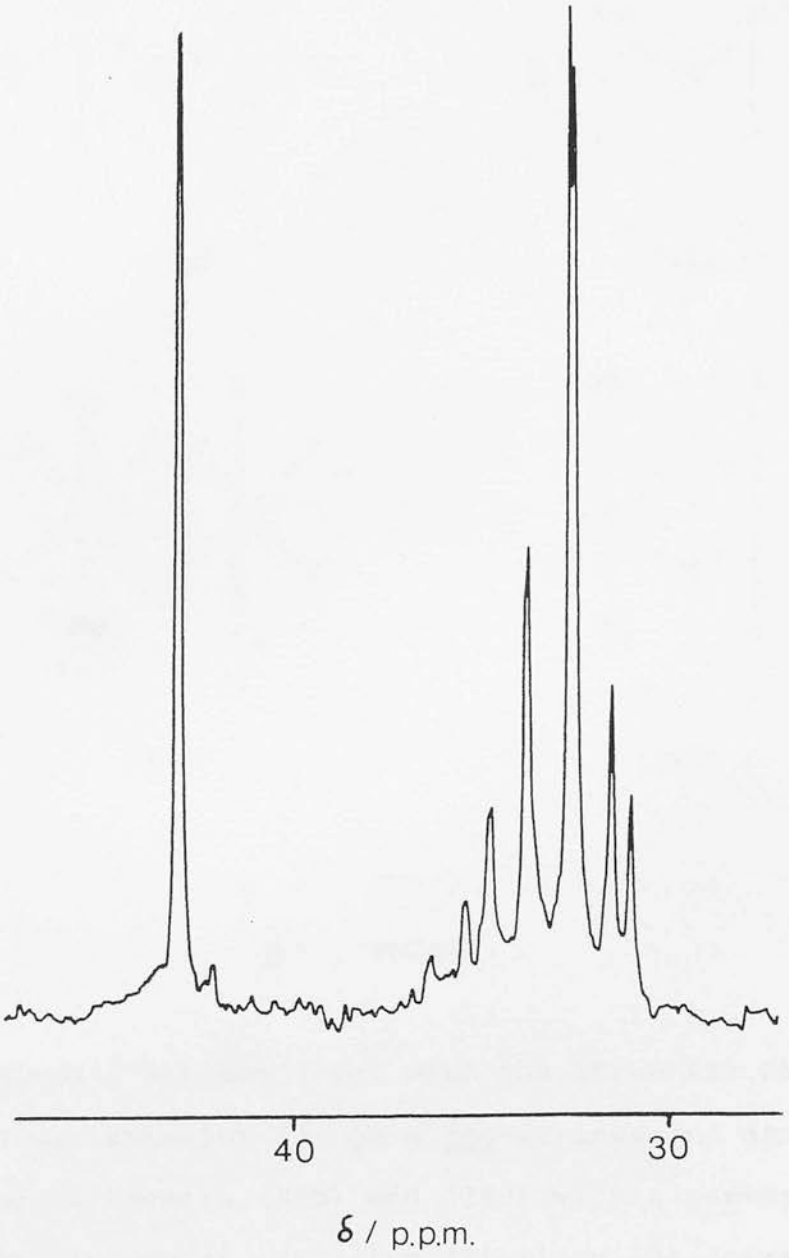
A stirred CH_2Cl_2 solution of $Ru_2Cl_5(PEt_2Ph)_4$ with an excess of phenylacetylene and $NaBH_4$ changes steadily from green to brown over 3 days. The brown solid isolated from the solution is non-conducting in CH_2Cl_2. The i.r. spectrum shows a $\nu_{C\equiv C}$ band at 1940 cm^{-1}, (2100 cm^{-1} for free phenylacetylene), and terminal and bridging ν_{Ru-Cl} vibrations at 330 and 250 cm^{-1} respectively. Analysis figures for this solid, although somewhat variable due to the presence of small amounts of solvent of

crystallisation, are persistently higher with respect to carbon and hydrogen than would be expected for complex (38).

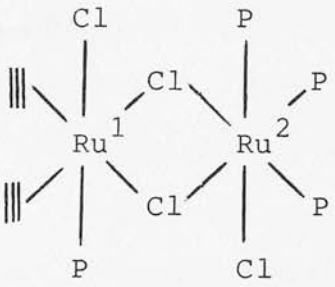
The presence of coordinated phenylacetylene is confirmed by the ^{1}H n.m.r. spectrum in CD_2Cl_2 at ambient temperature, showing a doublet at δ 4.8 p.p.m. (cf δ 4.7 p.p.m. for $[Ru_2Cl_3(PhC{\equiv}CH)(PEt_2Ph)_5]BF_4$, Chapter 2). The integrals of the ^{1}H n.m.r. signals suggest that the ratio of phenylacetylene to PEt_2Ph in this compound is 1:2 instead of 1:4 as expected for (38). Also the $^{31}P-[^{1}H]$ n.m.r. spectrum (Figure 3.2) consists of a singlet at δ 42.8 p.p.m. and an AB_2 pattern (δ_A = 34.5 p.p.m., δ_B = 31.9 p.p.m., $\Delta\nu_{AB}$ = 63.5 Hz, J_{AB} = 33.0 Hz) instead of the singlet and ABC pattern required for (38). On the basis of these data the complex has been formulated as the double-chloride-bridged species $(Et_2PhP)(PhC{\equiv}CH)_2ClRuCl_2RuCl(PEt_2Ph)_3$ (39).

The doublet structure of the coordinated phenylacetylene resonance in the ^{1}H n.m.r. spectrum therefore arises through coupling of the alkyne proton to the phosphorus nucleus of the single PEt_2Ph ligand attached to the same ruthenium centre (J_{PH} = 4.0 Hz), as confirmed by a heteronuclear decoupling experiment. The exact arrangement of ligands around each ruthenium centre is not known, so that various isomers are possible. An important feature of these isomers (39a,b,c,d) is that they all

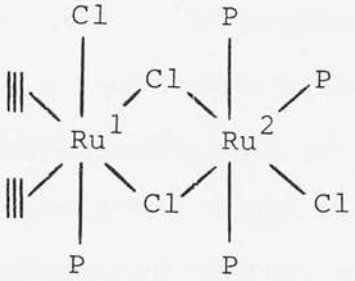
Figure 3.2. $^{31}P-[^{1}H]$ n.m.r. spectrum of $(Et_2PhP)(PhC{\equiv}CH)_2ClRuCl_2RuCl(PEt_2Ph)_3$ in $CDCl_3$



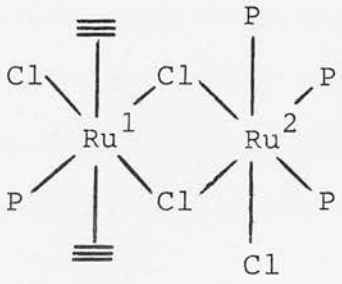
contain magnetically equivalent phenylacetylene ligands, as required by the ^{1}H n.m.r. spectral evidence.



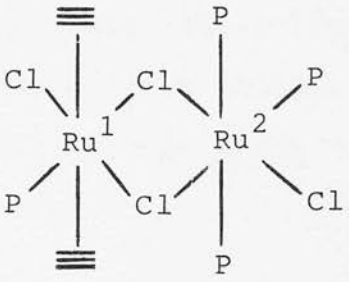
(39a)



(39b)



(39c)



(39d)

P = PEt_2Ph

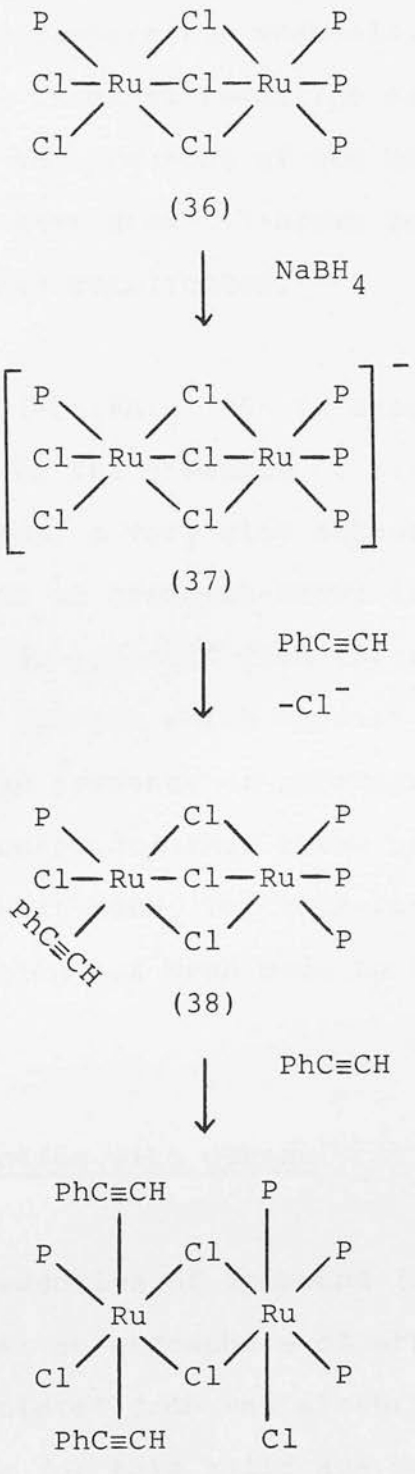
||| = $PhC{\equiv}CH$

Isomers (39a) and (39c) with the three PEt_2Ph ligands attached to ruthenium (2) in a fac-arrangement are preferred to isomers (39b) and (39d) with a mer-arrangement of PEt_2Ph ligands at ruthenium (2) since the former are considered to be more likely to give an AB_2 pattern in their $^{31}P-[^{1}H]$ n.m.r. spectra.

The mechanism of formation of this complex probably involves the initial reductive generation of the anion (37) followed by displacement of chloride ion by phenylacetylene to give the neutral species (38), which was the product originally sought. However, because alkynes have a high *trans* labilising effect and excess phenylacetylene is present, a second molecule of phenylacetylene could cleave the chloride bridge *trans* to the coordinated alkyne, giving the double-chloride-bridged product (39) (see Scheme 3.1). Such a mechanism implies that isomer (39c), with *trans*-alkyne ligands is produced, at least initially. Whether this isomer then rearranges to one with *cis*-alkyne ligands to relieve what would appear to be an inherent instability associated with having two π-acceptor ligands *trans* to each other is not known at this juncture.

It is interesting to compare this reaction with that described in Chapter 2 for the preparation of $[Ru_2Cl_3(PhC{\equiv}CH)(PEt_2Ph)_5]BF_4$ (23). In the latter case there is no evidence for the formation of a bis-alkyne species even though this mono-alkyne cation is very similar to the proposed intermediate (38) in having a phenylacetylene ligand *trans* to one of the bridging chlorides, rendering that chloride susceptible to displacement by another molecule of phenylacetylene. The difference in reactivity may be attributed to the replacement of a PEt_2Ph ligand in (23) by a terminal chloride in (38), resulting in greater electron density

Scheme 3.1 Proposed mechanism of formation of $(Et_2PhP)(PhC{\equiv}CH)_2ClRuCl_2RuCl(PEt_2Ph)_3$



P = PEt_2Ph

available at the ruthenium centre for back-donation to a second phenylacetylene ligand.

Attempts to prepare the mono-alkyne complex (38) by carrying out the chemical reduction of the mixed-valence complex (36) in the presence of one molar equivalent of phenylacetylene gave greenish-brown solids whose $^{31}P-[^{1}H]$ n.m.r. spectra are complicated.

When $Ru_2Cl_5(PEt_2Ph)_4$ (36) is treated with an excess of phenylacetylene in the presence of zinc amalgam or magnesium turnings, a very slow colour change (over several weeks) from green to greenish-brown is observed. The dark green-brown solids isolated from these reactions give $^{31}P-[^{1}H]$ n.m.r. spectra which consist of a few broad humps, indicative of the presence of paramagnetic species. From this it may be concluded that these reducing agents are far less efficient than $NaBH_4$ for this particular reaction. A similar observation has been made in the reaction with ethene.

3.2.2. The reaction with ethene

When the reduction of compound (36) with $NaBH_4$ is carried out under an atmosphere of ethene, an orange-brown solid can be isolated from the mixture after 3 days. Analysis figures for this solid are consistent with the formulation $(Et_2PhP)(C_2H_4)_2ClRuCl_2RuCl(PEt_2Ph)_3$ (40).

Terminal and bridging ν_{Ru-Cl} bands are observed in the i.r. spectrum at 300 and 240 cm^{-1} respectively. The $\nu_{C=C}$ band has not been identified.

The $^{31}P-[^{1}H]$ n.m.r. spectrum of a fresh solution of this complex in CD_2Cl_2 at ambient temperature consists of a singlet at δ 46.6 p.p.m. and an AB_2 pattern (δ_A = 35.90 p.p.m., δ_B = 34.9 p.p.m., $\Delta\nu_{AB}$ = 80.8 Hz, J_{AB} = 48.0 Hz) of relative intensity 1:3 (Figure 3.3).

The ^{1}H n.m.r. spectrum of a fresh solution of (40) in CD_2Cl_2 at ambient temperature shows, in addition to free ethene, which indicates some dissociation of the compound, two rather complex sets of resonances in the region normally associated with alkenes coordinated to ruthenium (II) (Figure 3.4). These resonances, centred at δ 3.8 and 3.2 p.p.m., suggest the presence of magnetically inequivalent ethene protons due to a preferred orientation of the ethene ligands. An alternative explanation is that the two ethene ligands (the integral values show an ethene to PEt_2Ph ratio of 1:2), are bound in an "asymmetric" fashion, i.e. <u>trans</u> to different types of ligand, unlike the phenylacetylene groups in compound (39). This, however, is considered less likely to give rise to the observed resonances which are roughly symmetrical about the mid-point between them, resembling an A_2B_2-type pattern. It is probable that complex (40) has one of the isomeric

Figure 3.3. $^{31}P-[^{1}H]$ n.m.r. spectrum of $(Et_2PhP)(C_2H_4)_2ClRuCl_2RuCl(PEt_2Ph)_3$ in CD_2Cl_2

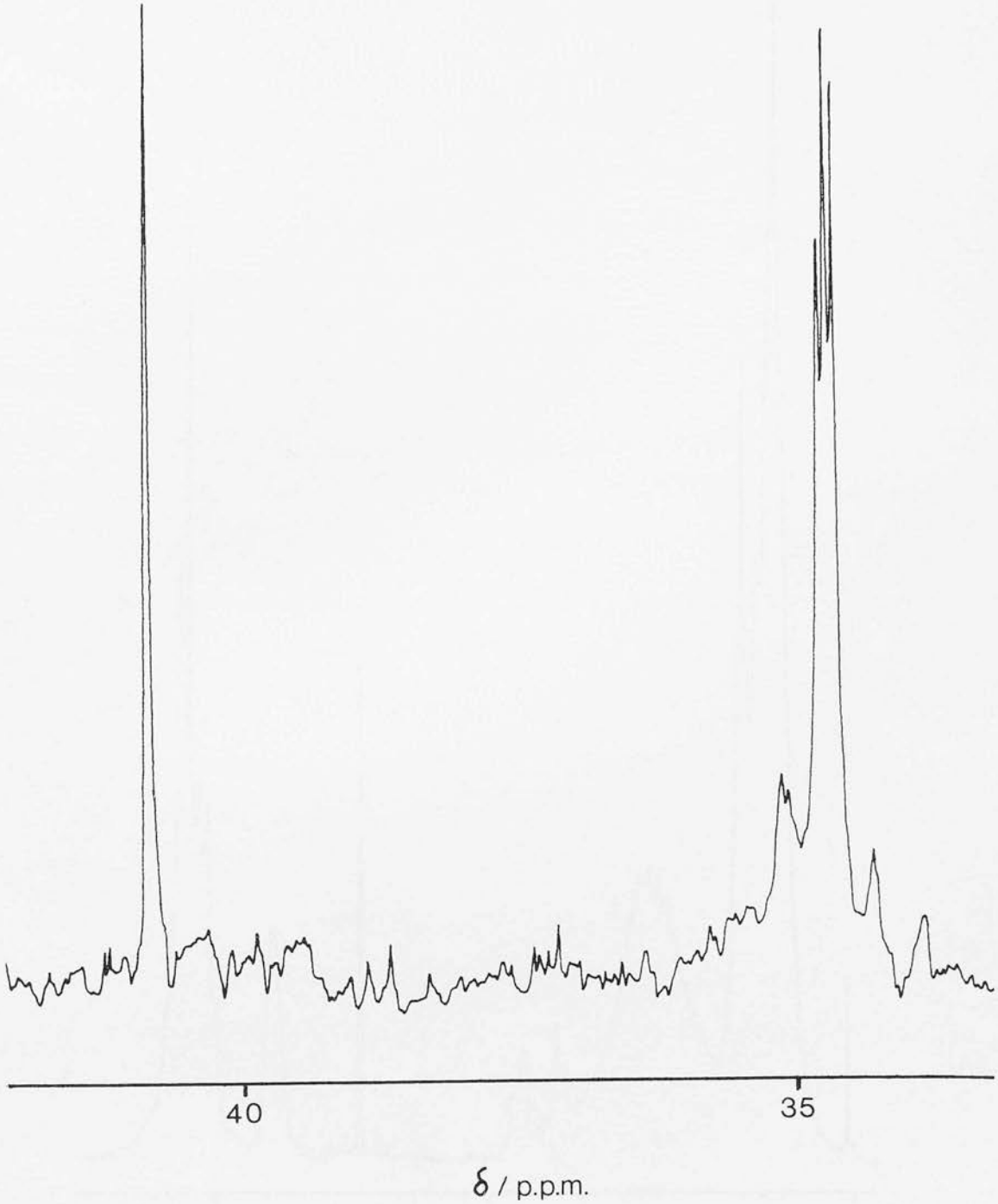
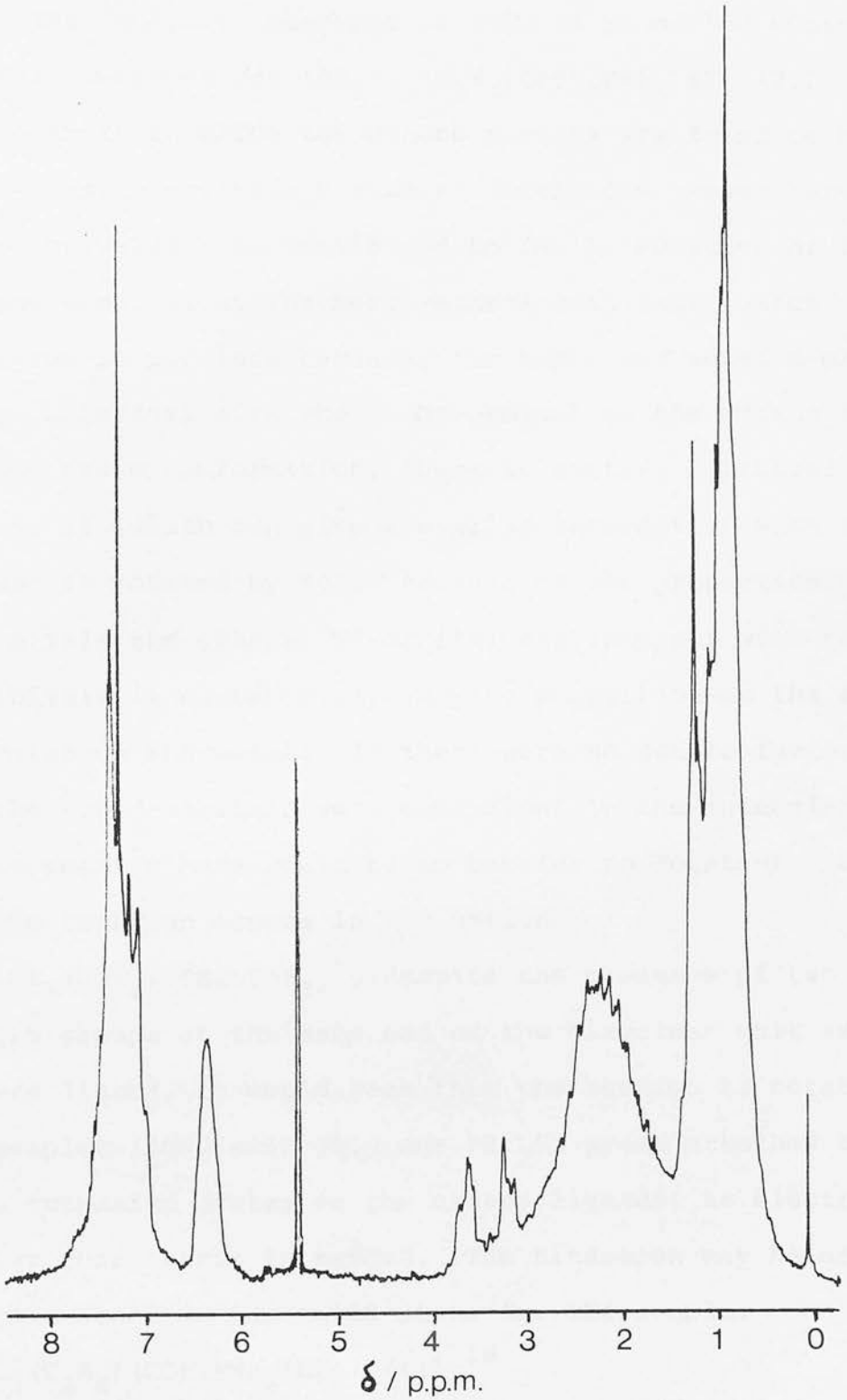
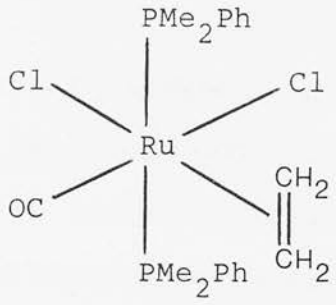


Figure 3.4. ^{1}H n.m.r. spectrum of $(Et_2PhP)(C_2H_4)_2ClRuCl_2RuCl(PEt_2Ph)_3$ in CD_2Cl_2



forms postulated for the bis-phenylacetylene complex (39) and is formed via an analogous reaction pathway (Scheme 3.1).

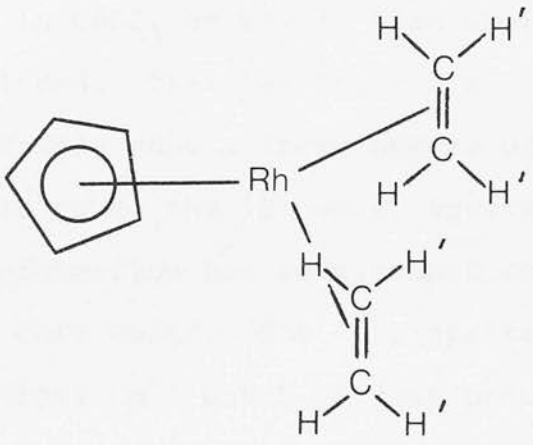
The ^1H n.m.r. spectrum of (40) is in marked contrast to that observed for $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22) (Chapter 2) in which the ethene protons are found to be magnetically equivalent even at fairly low temperatures. This equivalence is attributed to facile rotation of the ethene group about the metal-ethene bond axis. Such rotation is possible because, for any given metal d-orbital which interacts with the π^*-orbital of the ethene in the ground state conformation, there is another d-orbital at 90° to it, which can give a similar interaction when the ethene is rotated by 90°. Because of the properties of d-orbitals the ethene π^*-orbital can interact with both d-orbitals in continuously varying proportion as the angle of rotation increases. If there were no steric factor, and if the two d-orbitals were equivalent in the molecular environment, there would be no barrier to rotation. Since facile rotation occurs in the cation $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]^+$, despite the presence of two bulky PEt_2Ph groups at the same end of the binuclear unit as the ethene ligand, it would seem that the barrier to rotation in complex (40), with only one PEt_2Ph group attached to the same ruthenium centre as the ethene ligands, is electronic rather than steric in nature. The situation may be similar to that found in the solid state for the complex $RuCl_2(C_2H_4)(CO)(PMe_2Ph)_2$ (41).[19]



(41)

The C=C bond in this complex is essentially parallel to the Ru-P bonds. This preferred orientation of the ethene ligand has been accounted for as follows. Among the ligands bound to the ruthenium atom, the ethene and carbonyl ligands are good π-acceptors. If the C_2H_4 ligand lay in the same plane as the carbonyl group, then these ligands would compete for the same metal d-orbital for π-bonding purposes. With the C_2H_4 ligand nearly parallel to the Ru-P bonds, and hence essentially perpendicular to the Ru-C-O linkage, it interacts with a d-orbital which is not suitably positioned to interact with the CO ligand. Interestingly, the ethene ligand in this complex freely rotates in solution, even at 233K. The two ethene ligands in (40) may therefore be orientated in such a way that they do not compete for the same metal d-orbitals, even in solution. At the time of writing there are no known analogous complexes to (40) i.e. ruthenium (II) complexes containing two ethene ligands, so that no direct comparison can be made. There are, however, several rhodium(I) bis-alkene complexes, an example of which is

$Rh(C_2H_4)_2(\eta\text{-}C_5H_5)$.[107] The assumed instantaneous structure of this complex, (42), has four <u>endo</u> ethene protons and four <u>exo</u> ethene protons. At low temperatures (<253K) each set gives its own sharp multiplet signal in the ^1H n.m.r. spectrum, but as the temperature is raised, these broaden and coalesce, finally giving a single broad peak at 330K.



(42)

It has also been observed that $Rh(C_2H_4)_2(\eta\text{-}C_5Me_5)$ behaves similarly to $Rh(C_2H_4)_2(\eta\text{-}C_5H_5)$ but it has a somewhat higher coalescence temperature.[108] The iridium compound $Ir(C_2H_4)_2(\eta\text{-}C_5Me_5)$ shows inequivalent ethene proton resonances up to 383K, the barrier to rotation being almost entirely of electronic origin, since steric factors should be less restrictive about the larger metal atom.[109]

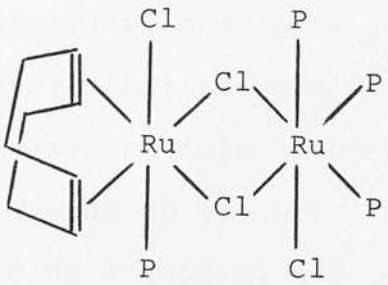
3.2.3. Preliminary reactions with other ligands (styrene, cod, CO, N_2)

When the reduction of (36) using $NaBH_4$ in CH_2Cl_2 is carried out in the presence of styrene a colour change from green to orange is observed after twelve days, (cf the reactions with ethene and phenylacetylene, which are complete after three days). The orange solid isolated from the solution is extremely unstable, giving green solutions when dissolved in $CDCl_3$ or CD_2Cl_2 even when air is rigorously excluded. The $^{31}P-[^1H]$ n.m.r. spectra of such solutions invariably show a large number of broad, poorly-resolved signals as do the ^1H n.m.r. spectra. Because of this, little information has been gained concerning the composition of this solid. The i.r. spectrum shows a strong band at 1945 cm^{-1} which is most probably due to one or more ruthenium-hydride vibrations (cf the reactions with phenylacetylene and ethene, which show no evidence for formation of hydride species in either the i.r. or ^1H n.m.r. spectra of the products). It would appear that, as in the $Ru_2Cl_4(PEt_2Ph)_5$ $/Tl^+$ reactions (Chapter 2), stable complexes of styrene are not formed. Comparison of this reaction with those carried out in the presence of CO or N_2, where only starting material was recovered even after several weeks (see later), indicate that the styrene is involved in some way, perhaps forming unstable intermediates with coordinated sytrene which then react further with $NaBH_4$ to give ruthenium (II) hydride species

which are also unstable.

Since the reactions with phenylacetylene and ethene readily give bis-alkyne and bis-alkene species, an obvious extension of this synthetic route involves the use of dienes such as 1,5-cyclooctadiene (cod). Thus, the reaction with cod gives an orange solution after 3 days from which can be isolated an orange/brown solid which is non-conducting in CH_2Cl_2. The i.r. spectrum shows $\nu_{C=C}$ at 1580 cm^{-1} and bands attributed to ν_{Ru-Cl} at 230, 310 cm^{-1}. The ^1H n.m.r. spectrum of this solid in $CDCl_3$ at room temperature indicates the presence of both free and coordinated alkene protons with signals at δ 5.6 and 3.8 p.p.m. respectively, the latter being extremely broad. No improvement in resolution has been observed on cooling the solution. Several resonances are present in the $^{31}P-[^1H]$ n.m.r. spectrum, suggesting a mixture of species. The most intense resonances are a singlet at δ 45.5 p.p.m. and what appears to be a poorly resolved AB_2 pattern at δ 31.0 p.p.m. Two smaller singlets are present at δ 52.9 and 44.7 p.p.m., along with what may be a second poorly resolved AB_2 pattern of half the intensity of that already mentioned and centred at δ 34.6 p.p.m. The broad nature of all the n.m.r. signals exhibited by this material, which do not vary with temperature, suggests the presence of a small amount of paramagnetic material. The reaction has been repeated several times and the above effect is observed in each case. Further characterisation of this

material has been prevented by the inability to separate these species. By comparison of the chemical shifts of the main $^{31}P-[^{1}H]$ n.m.r. signals with those of the bis-phenylacetylene and bis-ethene complexes it would appear likely that the main product is (43) or another isomer of that formulation.



$P = PEt_2Ph$

(43)

The presence of free alkene resonances in the ^{1}H n.m.r. spectrum suggest species with monodentate cod ligands are also present. The possibility that monomeric species are also formed should not be discounted since cod is known to take part in bridge cleavage reactions of the type shown in Equation 3.2.[110].

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl + 2cod \rightarrow 2RuCl_2(cod)(PEt_2Ph)_2 \quad ...3.2$$

Attempts to generate other double-chloride-bridged species with small π-bonding ligands such as CO or N_2 have been unsuccessful. Thus, when $Ru_2Cl_5(PEt_2Ph)_4$ is stirred in CH_2Cl_2 with an excess of $NaBH_4$ under an atmosphere of

either CO or N_2, the solution remains green even over a period of one month. The green solids isolated appear to consist mainly of the mixed-valence starting material.

3.2.4. Electrochemical studies

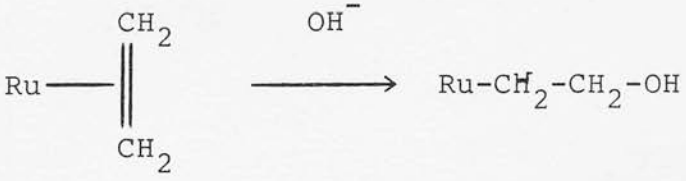
The cyclic voltammograms of the bis-ethene and bis-phenylacetylene complexes, (40) and (39), are poorly defined, exhibiting weak signals which correspond to several irreversible redox processes. No improvements have been observed on cooling the solutions. This has been found to be a general observation in electrochemical studies of doubly-chloride-bridged species of this type, unlike the well-defined processes associated with the triply-chloride-bridged complexes. The difference may be attributed to the greater inherent stability of the triple-chloride-bridged structures.

3.3. Reactions of the bis-ethene complex with nucleophiles.

When an evacuated, sealed n.m.r. tube containing a $CDCl_3$ solution of (40) is left to stand at ambient temperature for several days there are considerable changes in the ^1H and $^{31}P-[^1H]$ n.m.r. spectra. The ^1H n.m.r. spectrum shows, in addition to the resonances already mentioned, a sharp triplet at δ 3.7 p.p.m. and a broader triplet at δ 2.6 p.p.m., the latter exhibiting some poorly

resolved fine structure (Figure 3.5). A coupling constant of 6.2 Hz is observed for both these triplets. Also present is a small broad resonance at ca δ 4.5 p.p.m. No hydride resonances are observed at this stage. The $^{31}P-[^{1}H]$ n.m.r. spectrum shows the growth of a broad peak at δ 45.6 p.p.m. and a sharp singlet at δ 44.2 p.p.m. along with a broadening of the original AB_2 pattern of (40). No significant change is observed in this spectrum on cooling the solution.

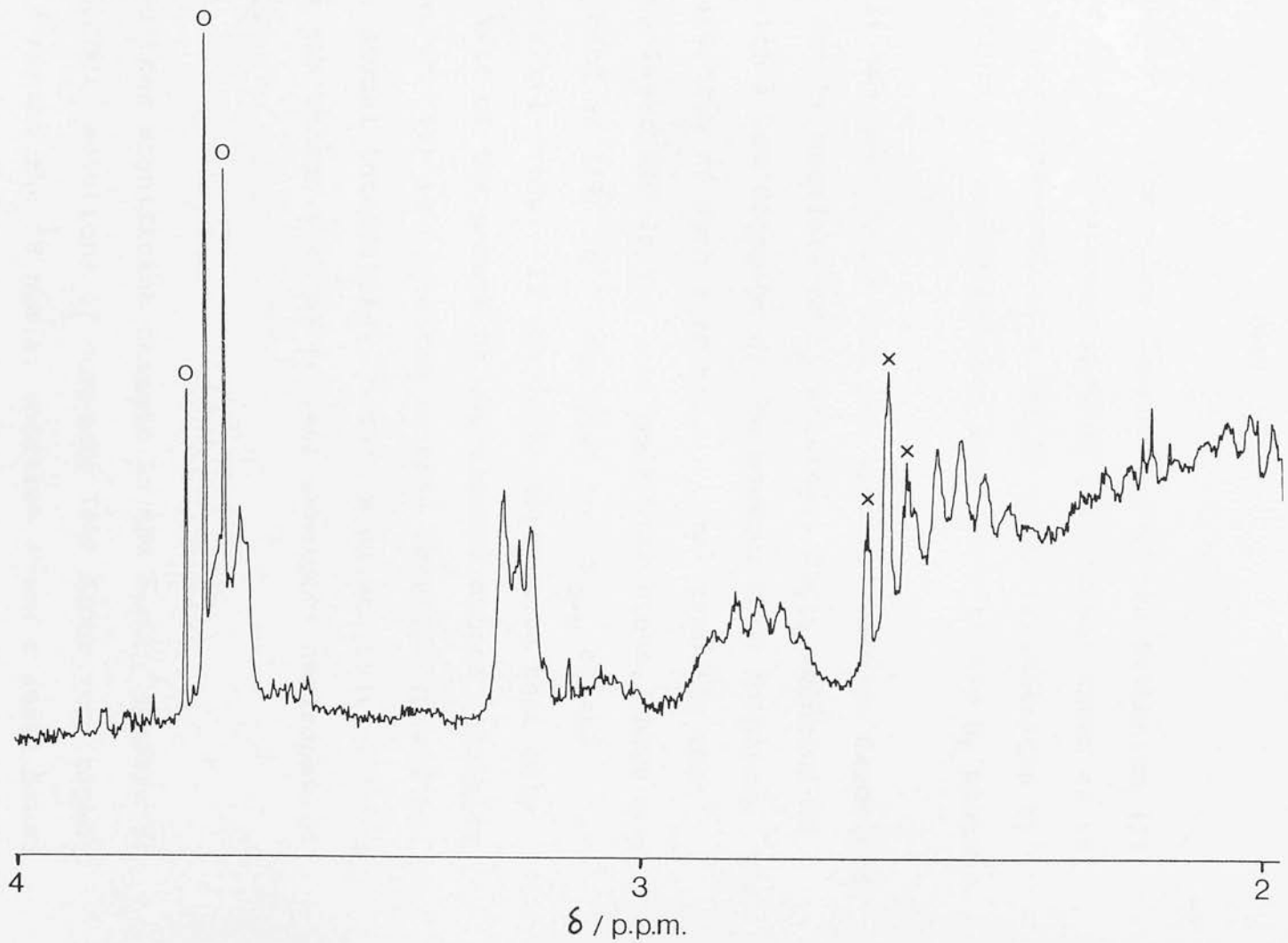
A tentative explanation for these changes involves the formation of a β-hydroxoethyl complex by nucleophilic attack of hydroxide ion on a coordinated ethene group of the starting material (Equ. 3.3.).

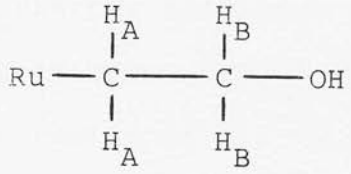


... 3.3

The hydroxide ion presumably comes from trace amounts of water in the solvent. Thus the triplet at δ 2.6 p.p.m. in the ^{1}H n.m.r. spectrum may be attributed to the H_A protons in (44) and the triplet at δ 3.7 p.p.m. to the H_B protons. The broad resonance at δ 4.5 p.p.m. is assigned to the hydroxy group proton.

Figure 3.5 ^{1}H n.m.r. spectrum of $(Et_2PhP)(C_2H_4)_2ClRuCl_2RuCl(PEt_2Ph)_3$ after one week at ambient temperature in $CDCl_3$





(44)

The nature of the other ligands around the ruthenium (II) centre in the postulated species (44) is not known as yet although the presence of a PEt_2Ph group is indicated by fine structure on the triplet attributed to the H_A protons.

It has been found that the spectral changes described above can be accelerated by shaking a $CDCl_3$ solution of (40) with a few drops of dilute aqueous NaOH solution. The i.r. spectrum of such a solution, after removing the aqueous layer and drying over molecular sieve, shows a sharp band at 3596 cm^{-1}, assigned to ν_{O-H} of the hydroxoalkyl group. It should be emphasised that only about half of the amount of coordinated ethene initially present in (40) is converted in this reaction (based on ^1H n.m.r. signal intensities). This suggests that only one of the two ethene ligands in (40) undergoes nucleophilic attack.

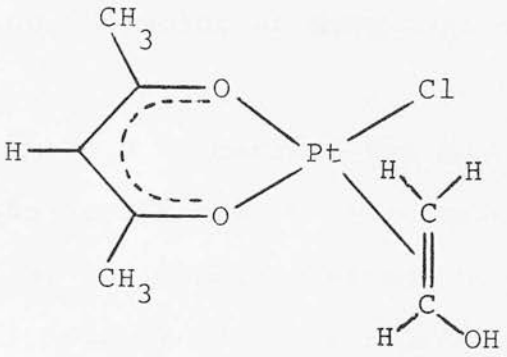
Further significant changes in the n.m.r. spectra of sealed $CDCl_3$ solutions of compound (40) occur very slowly. After 4 months the ^1H n.m.r. spectrum shows a small broad resonance at δ 8.7 p.p.m., a larger broad resonance at

δ 5.9 p.p.m., a sharper resonance at δ 5.3 p.p.m. and another small broad resonance at δ -5.0 p.p.m. The first of these is in a region of the ^{1}H n.m.r. spectrum where only a few classes of organic compound normally resonate. In the present context the most plausible assignment is to an aldehydic proton. Ethanal is the most likely candidate although this usually gives a resonance at ca δ 9.6 p.p.m. in the free state. It may be that ethanal is present but is in equilibrium with some other species. The equilibrium shown in Equ. 3.4 (keto-enol tautomerism) normally lies well to the left but it is possible that the position of equilibrium could be shifted by coordination of the enol form (vinyl alcohol) to a metal ion through the carbon-carbon double bond.

... 3.4

ethanal vinyl alcohol

Such complexes are known to exist e.g. $PtCl(CH_2{=}CHOH)(acac)$ (45), the structure of which has been confirmed by X-ray analysis.[111]



(45)

The ^{1}H n.m.r. spectrum of (45) shows an AX_2 set of resonances for the vinyl protons with a triplet at δ 7.2 p.p.m. and a doublet at δ 3.9 p.p.m. (J = 5Hz).[112]

It therefore seems possible that in the present case the resonances observed at δ 8.7, 5.9 and 5.3 p.p.m. are averaged resonances resulting from an equilibrium between free ethanal and coordinated vinyl alcohol.

If ethanal is indeed being formed in aged solutions of (40) it probably involves a β-hydride elimination from the postulated β-hydroxoethyl species (44). The presence of the resonance at δ -5.0 p.p.m. in the ^{1}H n.m.r. spectrum of the solution thought to contain ethanal suggests that the hydride is transferred to a ruthenium (II) centre. As already mentioned this process appears to take place very slowly and even after 6 months the ^{1}H n.m.r. resonances attributed to the β-hydroxoethyl species are still present although of greatly reduced intensity. Attempts to increase the rate of the proposed β-hydride transfer step

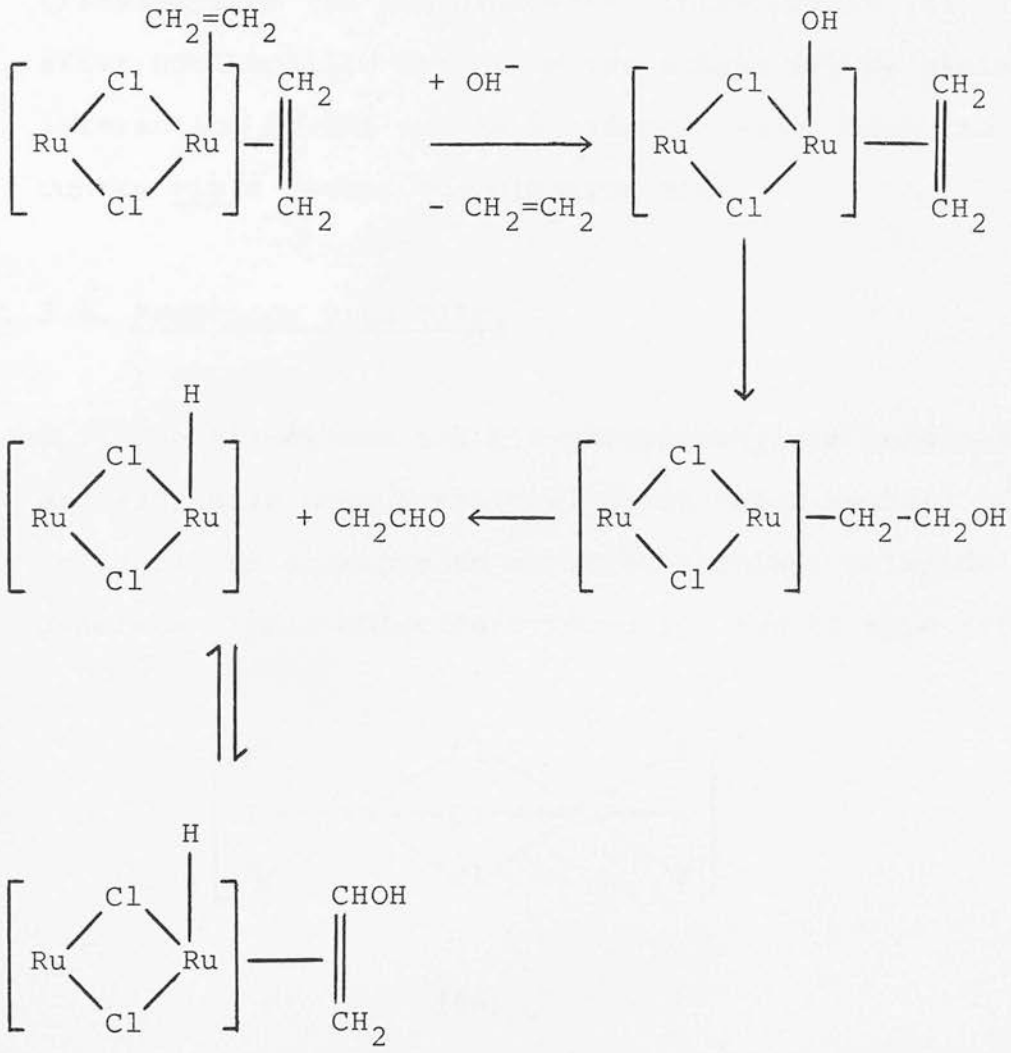
by heating the solution have been unsuccessful.

Scheme 3.2 summarises the reaction pathway which has been postulated based on these spectroscopic observations. The initial nucleophilic attack on coordinated ethene may be facilitated by prior coordination of hydroxide ion or water to (40) *via* displacement of one of the ethene ligands, which are already known to be in equilibrium with free ethene in $CDCl_3$ solution at room temperature.

It should be noted that at no stage has vinyl chloride been observed in this study, the production of which may conceivably arise through intramolecular attack of chloride ion on coordinated ethene in the complex (40). Even on addition of an excess of chloride ion to solutions of (40), no vinyl chloride is observed in the ^1H n.m.r. spectra.

The difference in reactivity towards nucleophiles (OH^-/H_2O) between the bis-ethene complex (40) and $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (22) (Chapter 2) may be attributed to two factors. Evidently the absence of a terminal chloride ligand on the ethene-bearing ruthenium (II) centre of the latter species renders that centre less electron-rich and therefore more susceptible to nucleophilic attack i.e. ligand displacement is favoured over ligand modification. Secondly complex (40) has two ethene ligands which are known to be in equilibrium with free ethene at ambient temperature in CD_2Cl_2 solution.

Scheme 3.2 Tentative reaction sequence for the production of ethanal from $(Et_2PhP)(C_2H_4)_2ClRuCl_2RuCl(PEt_2Ph)_3$ in the presence of OH^-

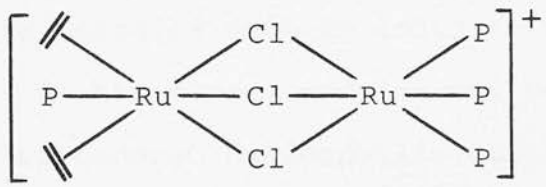


[n.b. the distribution of the other ligands around the metal centres in the unit represented by [Ru<Cl Cl>Ru] is not known. Also, it has been assumed that the chloride bridges remain intact throughout this proposed reaction pathway.]

This is important for two reasons. It may allow prior coordination of the nucleophile by displacement of one molecule of ethene, facilitating attack on the remaining ethene ligand. Furthermore, the postulated β-hydride transfer from the β-hydroxoethyl intermediate (44) formed after nucleophilic attack on the ethene may be assisted by interaction of one of the β hydrogen atoms with the metal centre via a vacant coordination site.

3.4. Reactions with $TlBF_4$

The bis-ethene and bis-phenylacetylene complexes (40) and (39) have been treated with equimolar amounts of $TlBF_4$ in CH_2Cl_2 in attempts to abstract terminal chloride and generate triple-chloride-bridged species of type (46).



(46)

The products which have been isolated from these reactions show a large number of resonances in their $^{31}P-[^{1}H]$ n.m.r. spectra, suggesting mixtures of species. The ^{1}H n.m.r. spectra show no evidence for coordinated ethene or phenylacetylene. The lack of success in these reactions may be attributed to the instability of cationic species of

the type desired in which two strong π-acceptor ligands are present.

3.5. Conclusions

The mixed-valence complex $Ru_2Cl_5(PEt_2Ph)_4$ has been shown to undergo reduction and loss of one terminal chloride ligand when treated with $NaBH_4$ and an excess of L in CH_2Cl_2 to yield asymmetric double-chloride-bridged complexes of the type $(Et_2PhP)L_2ClRuCl_2RuCl(PEt_2Ph)_3$ (L = ethene, phenylacetylene). Preliminary analogous experiments with L = CO, N_2, styrene and cyclooctadiene indicate that the above reaction is restricted to only those ligands L of appropriate electronic and steric character.

Initial studies seem to indicate that the coordinated ethene in the bis-ethene complex may be sufficiently activated to undergo nucleophilic attack by hydroxide ion to give a β-hydroxoethyl complex. This reaction, which takes place fairly rapidly in the presence of added hydroxide ion, also occurs, albeit more slowly, when only trace amounts of water are present. In both cases only partial conversion appears to take place, some unreacted coordinated ethene remaining even after extended periods.

The postulated β-hydroxoethyl complex appears to undergo further, slow, reaction to give some ethanal, which

is proposed to be in equilibrium with a coordinated vinyl alcohol complex. It is thought that both the initial nucleophilic attack on the ethene and the β-hydride elimination from the β-hydroxoethyl group are assisted by the availability of a vacant coordination site arising from facile dissociation of the second ethene ligand.

No evidence has been found for the formation of vinyl chloride from the bis-ethene complex, even in the presence of a large excess of free chloride ion.

3.6. Experimental Methods

Physical measurements were performed as described in Chapter 2.

Materials

The complex $Ru_2Cl_5(PEt_2Ph)_4$ was prepared as described in the literature.[18] $NaBH_4$ (Fisons) was dried at 40°C *in vacuo* before use.

$(Et_2PhP)(PhC{\equiv}CH)_2ClRuCl_2RuCl(PEt_2Ph)_3$ (39)

The compound $Ru_2Cl_5(PEt_2Ph)_4$ (0.50g, 0.48 mmol), $NaBH_4$ (0.25g, 6.58 mmol) and phenylacetylene (0.25g, 2.45 mmol) were stirred in degassed, dried CH_2Cl_2 (20 cm^3) under N_2 for 3 days. Excess $NaBH_4$ was filtered from the brown solution

under N_2. The solvent was removed from the filtrate *in vacuo* and the resulting brown oil triturated with degassed n-hexane to give a brown powder which was stored under N_2. (0.54g, 93%)

Found: C, 57.6; H, 5.8. Calc. for $C_{56}H_{72}Cl_4P_4Ru_2$: C, 55.4; H, 5.9%.

Mull i.r. spectrum : $\nu_{C\equiv C}$ 1940 (m), ν_{Ru-Cl} 250, 330 (m) cm^{-1}.

$(Et_2PhP)(C_2H_4)_2ClRuCl_2RuCl(PEt_2Ph)_3$ (40)

The compound $Ru_2Cl_5(PEt_2Ph)_4$ (0.50g, 0.48 mmol) and $NaBH_4$ (0.25g, 6.58 mmol) were stirred in degassed, dried CH_2Cl_2 (20 cm^3) under an atmosphere of ethene for 3 days. After filtering off excess $NaBH_4$ the orange-brown solution was worked up as for compound (39) to give an orange-brown solid. All operations were carried out under an atmosphere of C_2H_4 and the product was stored under C_2H_4. (0.47g, 92%)

Found: C, 50.1, H, 7.0. Calc. for $C_{44}H_{68}Cl_4P_4Ru_2$: C, 50.0; H, 6.4%.

Mull i.r. spectrum: ν_{Ru-Cl} 240, 300 (m) cm^{-1}. ($\nu_{C=C}$ not observed).

CHAPTER 4

REACTIONS OF MONOMERIC AND BINUCLEAR RUTHENIUM(II) COMPLEXES WITH ALKENYL TERTIARY PHOSPHINES

CHAPTER 4

Reactions of Monomeric and Binuclear Ruthenium(II) Complexes with Alkenyl Tertiary Phosphines

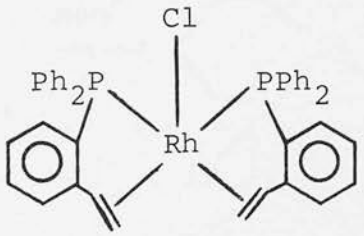
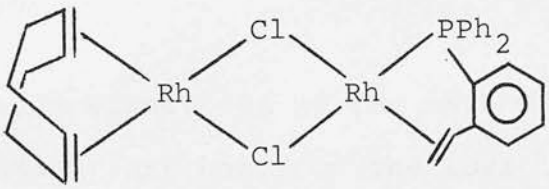
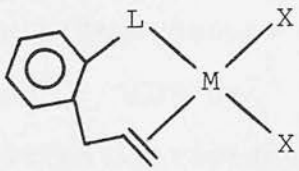
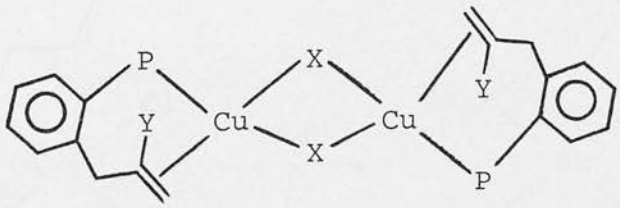
4.1 Introduction

In studying the reactivity of coordinated alkenes, tertiary phosphine and arsine ligands bearing "built-in" alkene substituents have proved extremely useful. There are several advantages associated with the use of these bidentate ligands. These include the ease of formation of metal-alkene complexes due to the chelating ability of the alkenyl phosphine which can bind to the metal through both the phosphorus atom and the alkene double bond. Furthermore if nucleophilic addition to the alkene occurs but does not result in a stable metal-carbon σ-bonded product the ligand is still attached *via* the phosphorus (or arsenic) atom. This "trapping" means that the complex may be isolated and the result of nucleophilic attack on the alkene characterised by conventional methods. For "ordinary" alkenes, characterisation of products of nucleophilic attack can be difficult, particularly when such products are volatile and present in very small amounts.

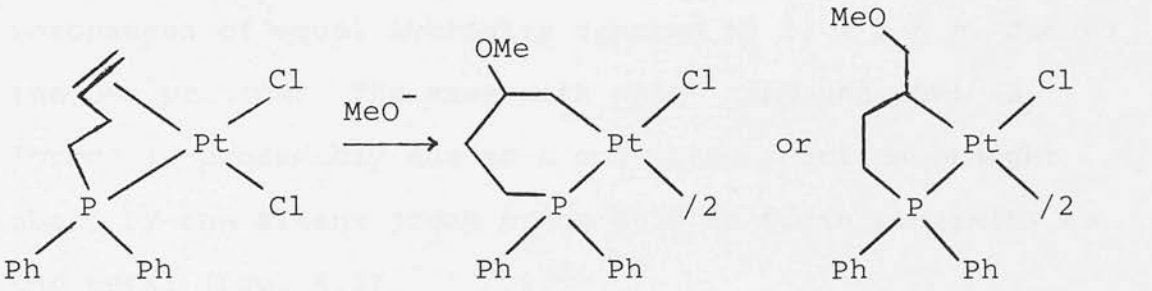
Some examples of transition metal complexes containing chelating alkenyl phosphines or arsines are given in Table 4.1.

The reaction of complex (47) (prepared from but-4-enyldiphenylphosphine and $PtCl_2(PhCN)_2$) with OMe^- provides a

Table 4.1. Transition metal complexes containing alkenyl phosphines and arsines

	Reference
	113
	113
$M(CO)_4SP$ M = Cr, Mo, W	114
	115
L = $As(CH_3)_2$ or $P(C_6H_5)_2$ M = Pd or Pt, X = Cl, Br	
	115b
(i) X = Cl, Br, I; Y = H (ii) X = Br; Y = CH_3	

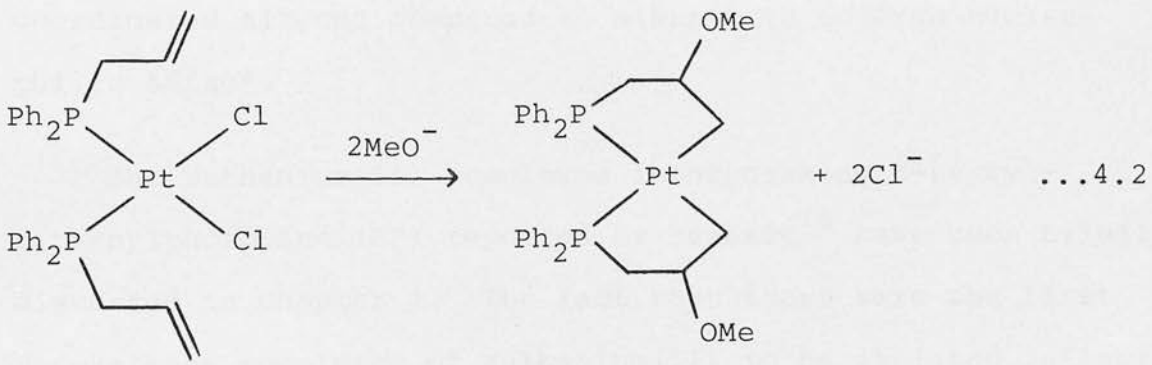
good example of nucleophilic attack on a coordinated alkene group (Equ. 4.1).[116]



(47) (48a) (48b) ...4.1

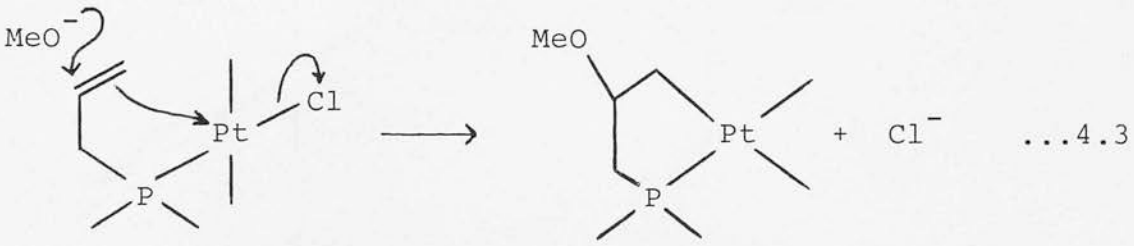
The suggested structures of the methoxy-substituted σ-bonded complex (48a,b) are based on the loss in the i.r. spectrum of the $\nu_{c=c}$ vibration of (47) at 1503 cm^{-1}, the presence of a new band at 1095 cm^{-1}, attributed to the OMe group, and ν_{Pt-Cl} (bridging) bands at 271 and 240 cm^{-1}.

Complex (49) has also been prepared.[116] Its i.r. spectrum shows that the alkene groups are not coordinated to the metal ($\nu_{c=c}$ = 1640 cm^{-1}; 1639 cm^{-1} for the free ligand) and its ^1H n.m.r. spectrum is virtually identical to that of the free ligand. Reaction of (49) with OMe^- gives a colourless complex formulated as (50) (Equ. 4.2).



(49) (50) ...4.2

It is probable that two geometrical isomers of (50), differing in the arrangement of the OMe groups (cis and trans with respect to the coordination plane of Pt), exist in the ratio 1:1, since the ^1H n.m.r. spectrum of (50) has two resonances of equal intensity centred at δ3.2 p.p.m. due to the OMe protons. The ease with which compound (50) is formed is presumably due to a concerted reaction brought about by the alkene group being held in close proximity to the metal (Equ. 4.3).

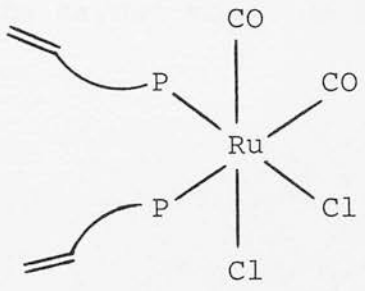


...4.3

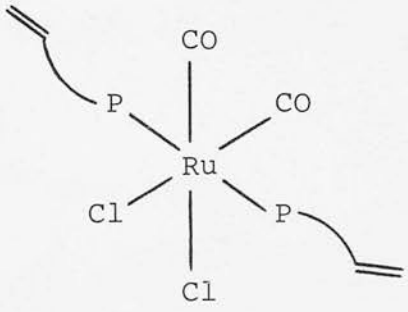
Chlorovinyl cyclic complexes (halogen-bridged) can be prepared by direct reaction of prop-2-ynyl-amines with $PdCl_2$ in the presence of LiCl.[117] In contrast, the addition of LiCl to methanolic solutions of allyldiphenylphosphine and $Na_2[PtCl_6]$ or $Na_2[PdCl_4]$ does not lead to nucleophilic attack on the alkene groups. Instead complex (49) and its trans-palladium analogue are obtained.[116] This difference in reaction is attributed to the greater susceptibility of coordinated alkynes compared to alkenes to undergo nucleophilic attack.

The ruthenium(II) complexes incorporating o-styryldiphenylphosphine (SP) reported by Bennett[16] have been briefly discussed in Chapter 1. The fact that these were the first mono-alkene complexes of ruthenium(II) to be isolated reflects

the ease with which metal-alkene complexes may be prepared, using bidentate ligands of this nature. Bennett's SP complexes undergo several interesting reactions. For example, the coordinated alkene groups in $RuCl_2(SP)_2$ are displaced by carbon monoxide to give geometrical isomers (51a,b) of $RuCl_2(CO)_2(SP)_2$ in which SP behaves as a monodentate phosphorus-bonded ligand.[16]

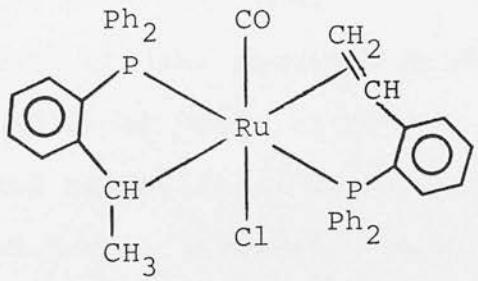


(51a)



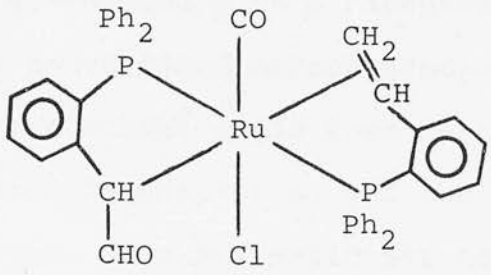
(51b)

Heating a solution of (51a) or (51b) for 2 hours in 2-methoxyethanol resulted in loss of some CO and chloride to give complex (52), which contains a bidentate SP ligand and a metal-carbon σ-bond in a five-membered chelate ring.[118]



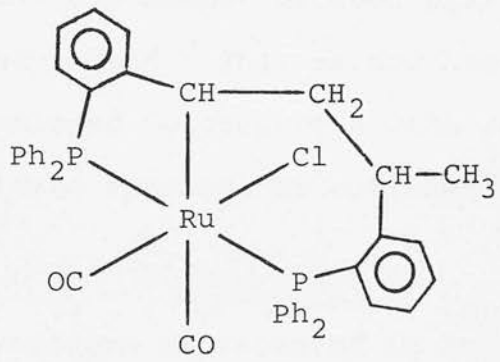
(52)

Also isolated from this reaction was complex (53), derived formally from (52) by oxidation of the methyl group to an aldehyde function.



(53)

Treating a solution of (53) in refluxing 2-methoxyethanol with carbon monoxide for 4-5 hours then gave complex (54).[118]



(54)

The mechanism for the formation of these complexes is uncertain, but may involve intermediate ruthenium(II) hydride species. There is also the possibility that (53) arises by some ruthenium(III) or (IV) promoted oxidation of one of the vinyl groups of (51a) or (51b) to give a CH_2CHO group (cf the $PdCl_2$ promoted oxidation of terminal alkenes to aldehydes or ketones in the Wacker process), which then eliminates HCl at the internal carbon atom to form the Ru-C chelate σ-bonded ring.

The aim of the work presented in this chapter was to prepare binuclear triple-chloride-bridged ruthenium complexes with one or more alkenyl tertiary phosphine ligands occupying

terminal positions, hopefully in a bidentate manner. The reactivity of the coordinated alkene groups in such complexes towards nucleophilic attack could then be studied, as for the ethene complexes in Chapter 2, and the products of such attack characterised. Two synthetic strategies were used to achieve the initial aim of preparing suitable complexes for study:

(a) Intermolecular coupling reactions of pairs of monomeric species, with at least one member of each pair containing the alkenyl phosphine ligand. This method has previously been successfully employed to prepare a wide range of binuclear triply-bridged species, as outlined in Chapter 1, Section 1.4.1.

(b) In view of the success experienced in introducing various ligands into the complex $Ru_2Cl_4(PEt_2Ph)_5$ after abstraction of terminal chloride by $TlBF_4$, the same method could be used to incorporate alkene phosphines. Initial attachment would probably occur <u>via</u> the phosphorus atom, with displacement of a PEt_2Ph ligand by the alkene group occurring either unaided, or with the assistance of heat or u.v. irradiation.

4.2 <u>Synthesis of monomeric complexes of ruthenium(II) containing alkenyl phosphines</u>

The SP complexes described earlier were derived by treatment of "$RuCl_3.xH_2O$" with SP in various solvents.[16] In this work attempts were made to synthesise similar complexes

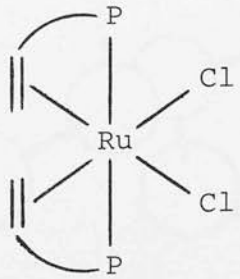
by reactions of alkenyl phosphines with various monomeric ruthenium(II) tertiary phosphine complexes.

4.2.1 Reactions of $RuCl_2(PPh_3)_3$ with alkenyl phosphines

4.2.1.1 Preparation and characterisation of $RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2$

Heating a suspension of $RuCl_2(PPh_3)_3$ in hexane with a six-fold excess of but-4-enyldiphenylphosphine, $Ph_2P(CH_2)_2CH{=}CH_2$, for 30 minutes yields a mustard coloured powder, which, on recrystallisation from CH_2Cl_2/MeOH, gives yellow crystals which are non-conducting in CH_2Cl_2 solution. The same product is obtained when the reaction is carried out in more polar solvents such as acetone.

A single crystal X-ray analysis of this complex revealed structure (55), a view of which is given in Figure 4.1. Some selected bond lengths and angles are given in Tables 4.2 and 4.3 respectively.



(55)

The increase in the length of the carbon-carbon double bond on coordination to the metal (1.40Å as compared to 1.25Å for the free alkene) is consistent with back-donation of electron

Figure 4.1 The structure of $RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2$ (55)

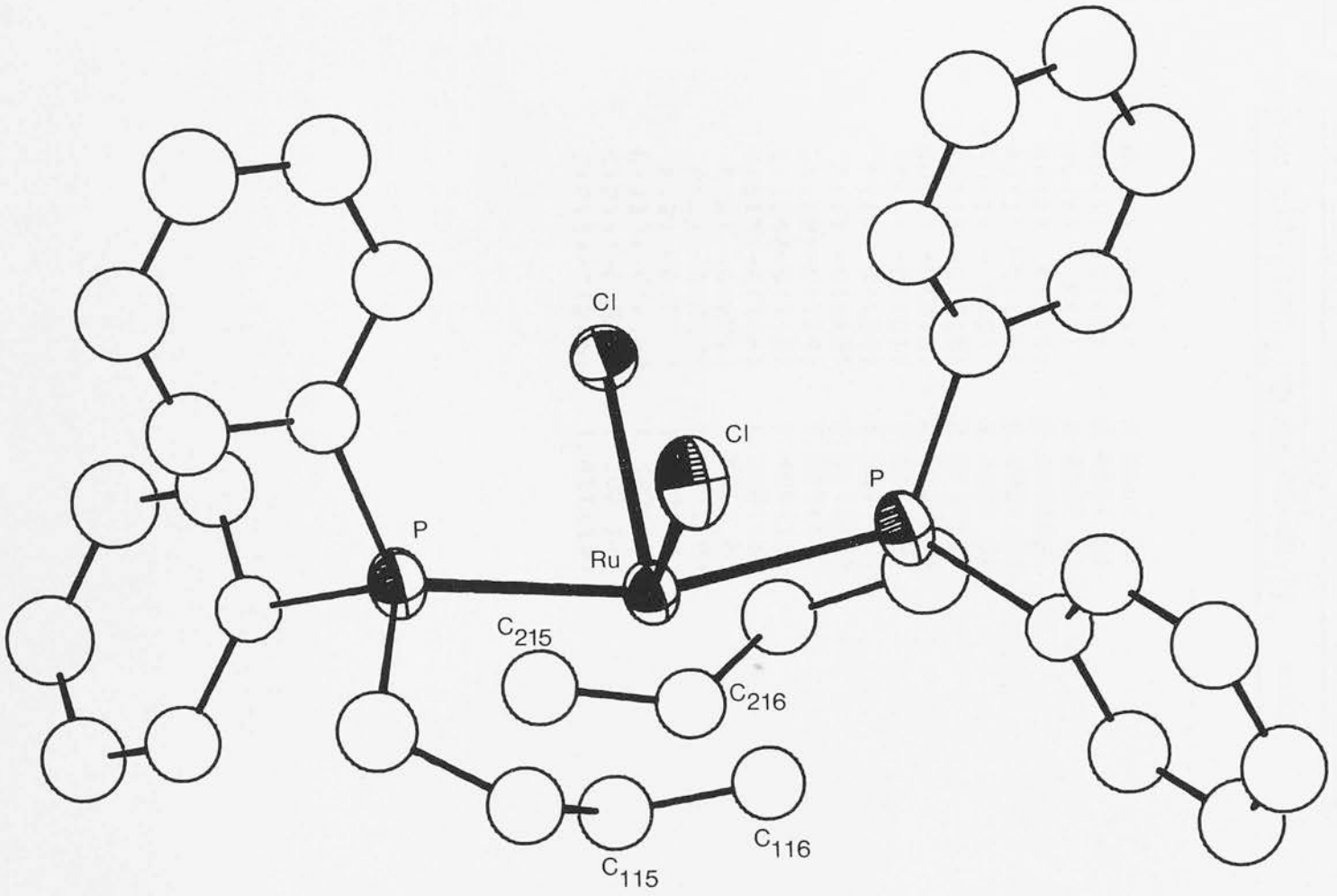


Table 4.2 Bond lengths (Å) with standard deviations for $RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2$ (55)

Ru(1) -Cl(1)	2.466(3)
Ru(1) -Cl(2)	2.450(3)
Ru(1) - P(1)	2.430(3)
Ru(1) -C(115)	2.219(13)
Ru(1) -C(116)	2.193(10)
Ru(1) - P(2)	2.423(3)
Ru(1) -C(215)	2.245(11)
Ru(1) -C(216)	2.212(9)
P(1) -C(101)	1.851(8)
P(1) -C(107)	1.837(8)
P(1) -C(113)	1.814(15)
C(113)-C(114)	1.515(18)
C(114)-C(115)	1.489(16)
C(115)-C(116)	1.380(16)
P(2) -C(201)	1.846(8)
P(2) -C(207)	1.859(8)
P(2) -C(213)	1.840(14)
C(213)-C(214)	1.522(17)
C(214)-C(215)	1.502(16)
C(215)-C(216)	1.411(14)

Table 4.3 Bond angles (degrees) with standard deviations for $RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2$ (55)

Cl(1)	-Ru(1)	-Cl(2)	95.38(11)	Ru(1)	- P(1)	-C(113)	105.5(5)
Cl(1)	-Ru(1)	- P(1)	88.12(11)	C(101)	- P(1)	-C(107)	99.7(4)
Cl(1)	-Ru(1)	-C(115)	161.9(3)	C(101)	- P(1)	-C(113)	105.2(5)
Cl(1)	-Ru(1)	-C(116)	161.3(3)	C(107)	- P(1)	-C(113)	105.7(6)
Cl(1)	-Ru(1)	- P(2)	80.88(10)	P(1)	-C(101)	-C(102)	123.6(6)
Cl(1)	-Ru(1)	-C(215)	89.2(3)	P(1)	-C(101)	-C(106)	116.4(6)
Cl(1)	-Ru(1)	-C(216)	82.86(24)	P(1)	-C(107)	-C(108)	117.6(6)
Cl(2)	-Ru(1)	- P(1)	81.24(11)	P(1)	-C(107)	-C(112)	122.3(6)
Cl(2)	-Ru(1)	-C(115)	90.9(3)	P(1)	-C(113)	-C(114)	111.0(9)
Cl(2)	-Ru(1)	-C(116)	83.9(3)	C(113)	-C(114)	-C(115)	110.8(10)
Cl(2)	-Ru(1)	- P(2)	87.43(10)	Ru(1)	-C(115)	-C(114)	115.0(8)
Cl(2)	-Ru(1)	-C(215)	161.6(3)	Ru(1)	-C(115)	-C(116)	70.8(7)
Cl(2)	-Ru(1)	-C(216)	161.38(24)	C(114)	-C(115)	-C(116)	124.6(11)
P(1)	-Ru(1)	-C(115)	76.0(3)	Ru(1)	-C(116)	-C(115)	72.8(7)
P(1)	-Ru(1)	-C(116)	110.1(3)	Ru(1)	- P(2)	-C(201)	118.3(3)
P(1)	-Ru(1)	- P(2)	163.41(11)	Ru(1)	- P(2)	-C(207)	121.3(3)
P(1)	-Ru(1)	-C(215)	116.7(3)	Ru(1)	- P(2)	-C(213)	106.7(4)
P(1)	-Ru(1)	-C(216)	80.18(24)	C(201)	- P(2)	-C(207)	98.6(4)
C(115)	-Ru(1)	-C(116)	36.4(4)	C(201)	- P(2)	-C(213)	106.9(5)
C(115)	-Ru(1)	- P(2)	116.5(3)	C(207)	- P(2)	-C(213)	103.5(5)
C(115)	-Ru(1)	-C(215)	90.2(4)	P(2)	-C(201)	-C(202)	117.2(6)
C(115)	-Ru(1)	-C(216)	85.8(4)	P(2)	-C(201)	-C(206)	122.4(6)
C(116)	-Ru(1)	- P(2)	80.4(3)	P(2)	-C(207)	-C(208)	123.4(6)
C(116)	-Ru(1)	-C(215)	86.1(4)	P(2)	-C(207)	-C(212)	116.5(6)
C(116)	-Ru(1)	-C(216)	103.6(4)	P(2)	-C(213)	-C(214)	109.4(9)
P(2)	-Ru(1)	-C(215)	75.7(3)	C(213)	-C(214)	-C(215)	111.8(9)
P(2)	-Ru(1)	-C(216)	110.46(24)	Ru(1)	-C(215)	-C(214)	114.2(7)
C(215)	-Ru(1)	-C(216)	36.9(4)	Ru(1)	-C(215)	-C(216)	70.3(6)
Ru(1)	- P(1)	-C(101)	119.2(3)	C(214)	-C(215)	-C(216)	124.8(10)
Ru(1)	- P(1)	-C(107)	120.0(3)	Ru(1)	-C(216)	-C(215)	72.8(6)

density from the metal to the Π^* anti-bonding orbitals of the alkene.

The $^{31}P-\{^1H\}$ and ^1H n.m.r. spectra of this complex in $CDCl_3$ are consistent with retention of the solid state structure in solution. Thus, the former shows a temperature invariant singlet at δ45.2 p.p.m. A set of resonances between δ1.6 and 3.5 p.p.m. in the ^1H n.m.r. spectrum (Figure 4.2) is assigned to the protons of the coordinated alkene groups. No signals are observed in the region δ 4.9 to 6.0 p.p.m., characteristic of the free alkene (Figure 4.3). The complexity of the phenyl resonances of the complex as compared to those of the free ligand is probably due to restricted rotation about the Ru-P bond because of the chelating nature of the ligand. This results in the protons on one of the phenyl rings attached to the phosphorus atom being magnetically inequivalent to those on the other phenyl ring.

The electrochemistry of this complex (Figure 4.4) is interesting in that it consists of a reversible oxidation at +0.77V (*vs* Ag/Ag^+). The reversible nature of this oxidation step indicates that the cationic Ru(III) species $[RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2]^+$ is stable, at least on the electrochemical time scale. Bearing in mind the importance of metal to alkene back-bonding in complexes of this type and the usual inability of Ru(III) centres to achieve this effectively, the stability of the oxidised species must be attributed to the chelating nature of the alkenyl phosphine.

Figure 4.2 ^{1}H n.m.r. spectrum of $RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2$ (55) in $CDCl_3$

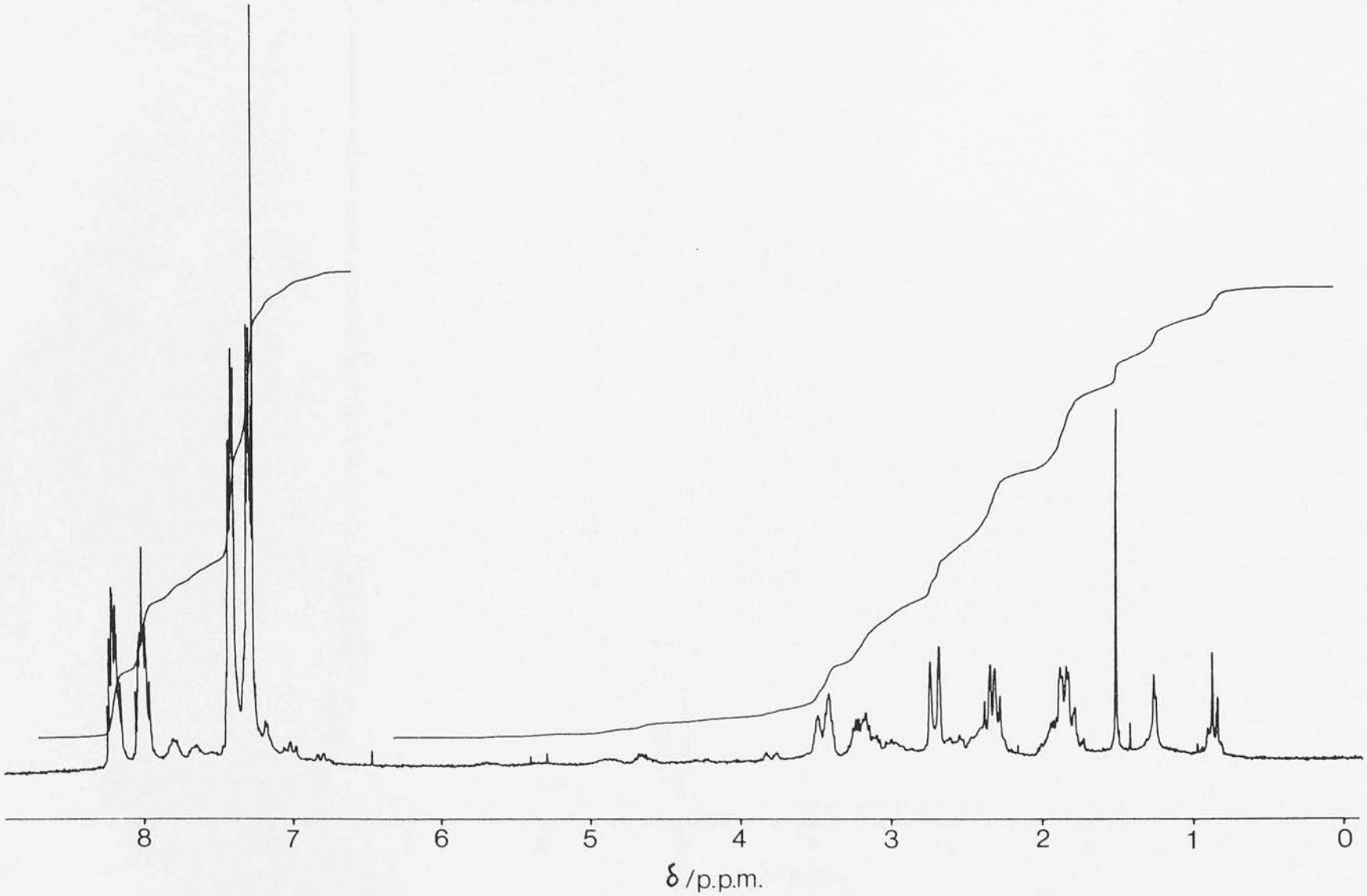


Figure 4.3 ^{1}H n.m.r. spectrum of $Ph_2P(CH_2)_2CH=CH_2$ in $CDCl_3$

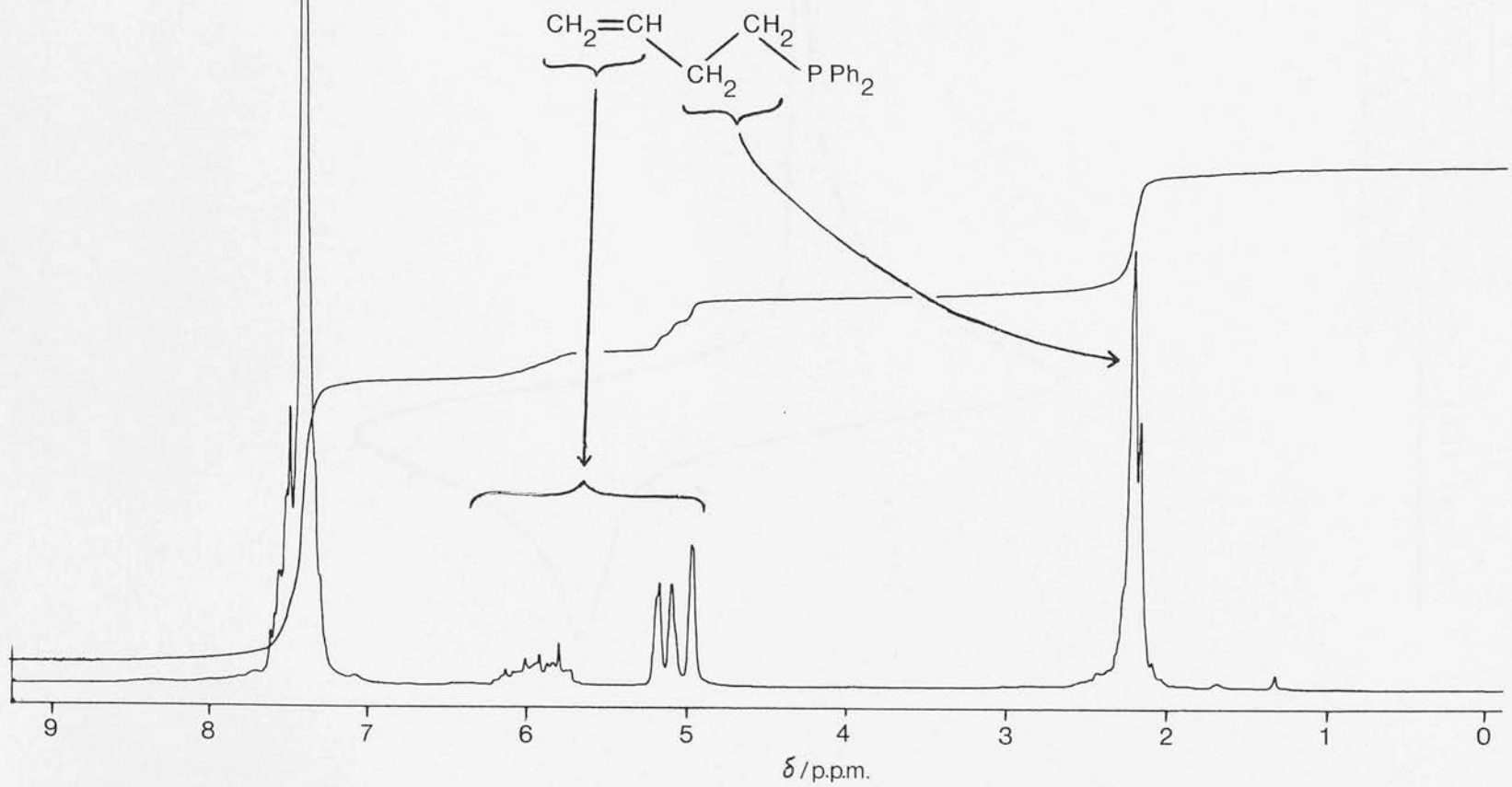
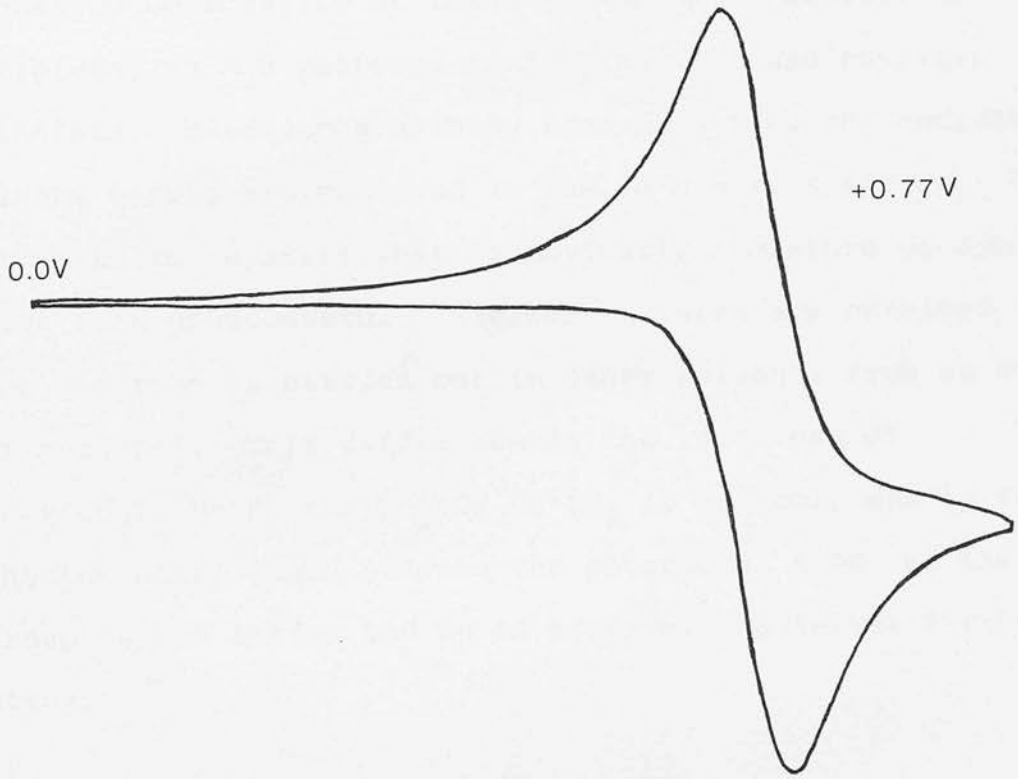


Figure 4.4 Cyclic voltammogram of $RuCl_2(PPh_2(CH_2CH_2CH{=}CH_2))_2$ (55) in 0.5M Bu_4NBF_4/CH_2Cl_2 *vs.* Ag/Ag^+



4.2.1.2 The reaction of $RuCl_2(PPh_3)_3$ with allyldiphenylphosphine

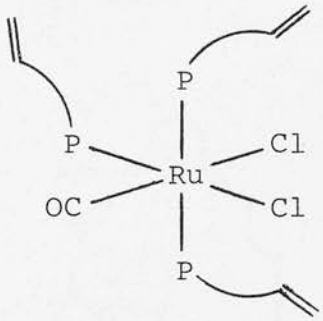
Reaction of $RuCl_2(PPh_3)_3$ with allyldiphenylphosphine, $Ph_2PCH_2CH=CH_2$, in refluxing hexane gives a light orange powder which conducts in CH_2Cl_2, indicating the presence of ionic species. The $^{31}P-\{^1H\}$ n.m.r. spectrum of this material in $CDCl_3$ consists of over thirty signals, from which it is possible to identify at least two sets of doublets and triplets, an A_2B pattern, an A_2B_2 pattern and numerous singlets. Resonances arising from both free and coordinated alkene groups are observed in the ^1H n.m.r. spectrum. All attempts to separate what is obviously a mixture of species have been unsuccessful. Similar mixtures are obtained when the reaction is carried out in other solvents such as acetone or methanol. This difference in the reactions of $Ph_2P(CH_2)_2CH=CH_2$ and $Ph_2PCH_2CH=CH_2$ is probably due to the shorter alkyl chain between the phosphorus atom and the alkene group in the latter and is an area which deserves further study.

4.2.2 Reactions of $RuCl_2(CO)(PPh_3)_2$dmf with alkenylphosphines

4.2.2.1 Preparation and characterisation of $RuCl_2(CO)(PPh_3)_x(PPh_2(CH_2CH_2CH=CH_2))_y$ (x = 1, y = 1; x = 0, y = 2,3)

When the carbonyl-containing complex $RuCl_2(CO)(PPh_3)_2$dmf (with trans chlorides and trans PPh_3 groups) is heated with an excess of $Ph_2P(CH_2)_2CH=CH_2$ in hexane a pale yellow solid

precipitates which is non-conducting in CH_2Cl_2. A single crystal X-ray analysis carried out on a crystal grown from CH_2Cl_2/hexane revealed structure (56).



(56)

It is suspected from the correspondence of y- and z-coordinates that the true crystal system of this crystal is monoclinic and that the data-collection crystal was twinned. At the time of writing this problem has not been resolved and the crystal data are presented as for a triclinic system, with two molecules of $RuCl_2(CO)(PPh_2(CH_2CH_2CH{=}CH_2))_3$ per asymmetric unit. A view of one of the molecules is given in Figure 4.5 and selected bond lengths and angles for both molecules are given in Tables 4-6, from which it can be seen that there are no significant differences between the two structures.

The $^{31}P-\{^1H\}$ n.m.r. spectrum of this complex in $CDCl_3$ consists of a triplet at δ31.1 p.p.m. and a doublet centred at δ16.1 p.p.m. with $^2J_{PP}$ = 24.4 Hz (Figure 4.6). As expected the ^1H n.m.r. spectrum exhibits only free alkene proton resonances (δ4.5 to 6.0 p.p.m.). The i.r. spectrum contains an uncoordinated $\nu_{C=C}$ vibration at 1633 cm^{-1} and a $\nu_{C\equiv O}$ band at 1958 cm^{-1} (*cf.* 1911 cm^{-1} for $RuCl_2(CO)(PPh_3)_2dmf$).

Figure 4.5 Structure of $RuCl_2(CO)(PPh_2(CH_2CH_2CH{=}CH_2))_3$ (56)

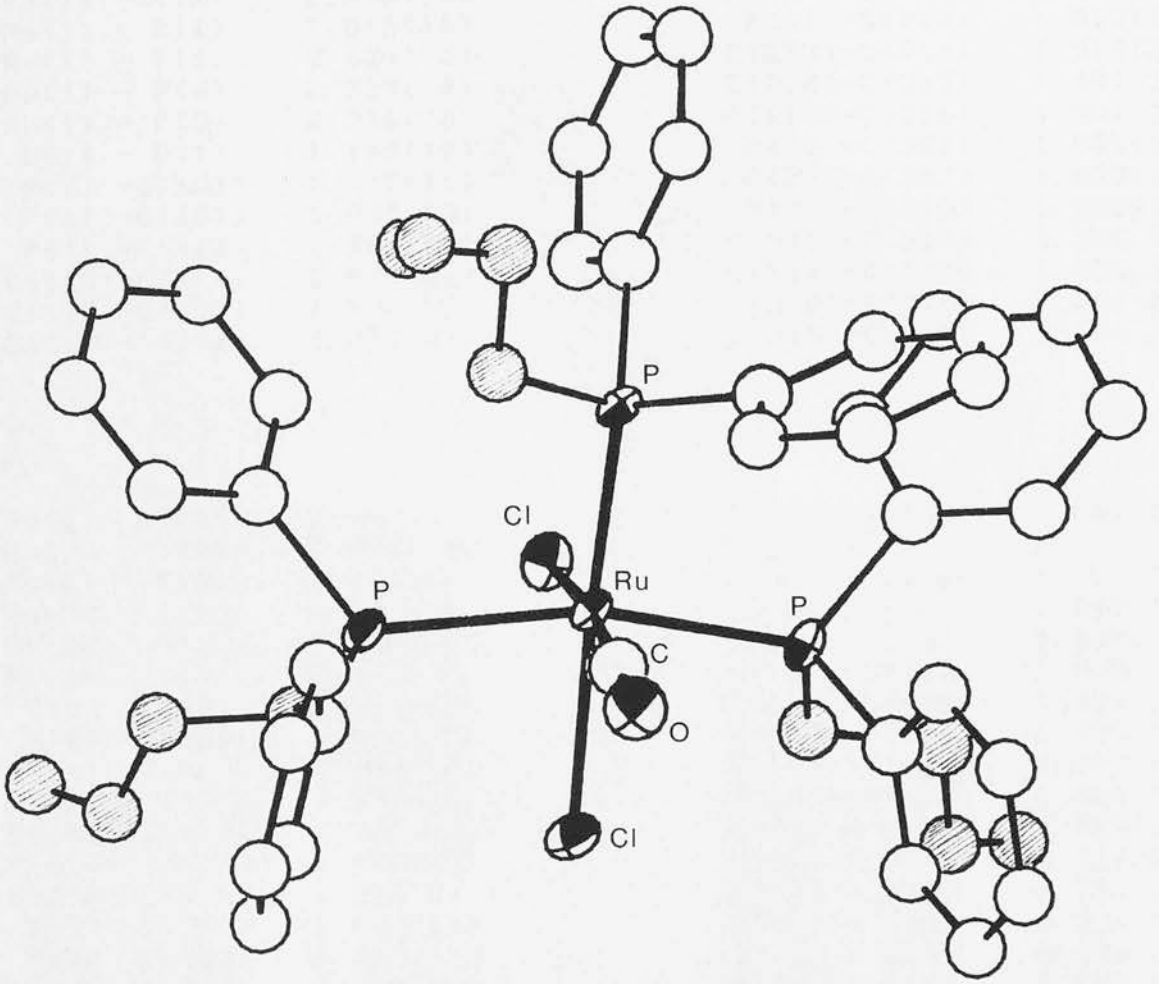


Table 4.4 Bond lengths (Å) with standard deviations for $RuCl_2(CO)(PPh_2(CH_2CH_2CH{=}CH_2))_3$ (56)

Molecule 1

Ru(1) -Cl(1)	2.460(4)	P(2) -C(201)	1.849(12)
Ru(1) -Cl(2)	2.453(4)	P(2) -C(207)	1.854(11)
Ru(1) - C(1)	1.816(16)	P(2) -C(213)	1.813(16)
Ru(1) - P(1)	2.424(5)	C(213)-C(214)	1.514(23)
Ru(1) - P(2)	2.355(4)	C(214)-C(215)	1.49(3)
Ru(1) - P(3)	2.396(5)	C(215)-C(216)	1.30(3)
C(1) - O(1)	1.148(19)	P(3) -C(301)	1.831(12)
P(1) -C(101)	1.819(11)	P(3) -C(307)	1.820(11)
P(1) -C(107)	1.837(12)	P(3) -C(313)	1.825(16)
P(1) -C(113)	1.834(15)	C(313)-C(314)	1.53(3)
C(113)-C(114)	1.479(21)	C(314)-C(315)	1.57(3)
C(114)-C(115)	1.52(3)	C(315)-C(316)	1.20(6)
C(115)-C(116)	1.27(3)	C(315)-C(317)	1.10(7)

Molecule 2

Ru(2) -Cl(3)	2.458(4)	C(513)-C(514)	1.547(23)
Ru(2) -Cl(4)	2.451(4)	C(514)-C(515)	1.47(3)
Ru(2) - C(2)	1.816(16)	C(515)-C(516)	1.23(3)
Ru(2) - P(4)	2.433(5)	P(6) -C(601)	1.819(11)
Ru(2) - P(5)	2.362(5)	P(6) -C(607)	1.809(12)
Ru(2) - P(6)	2.403(5)	P(6) -C(613)	1.824(16)
C(2) - O(2)	1.137(19)	C(613)-C(614)	1.52(3)
P(4) -C(401)	1.835(12)	C(614)-C(615)	1.57(3)
P(4) -C(407)	1.824(11)	C(615)-C(616)	1.20(5)
P(4) -C(413)	1.854(16)	C(615)-C(616)	1.25(7)
C(413)-C(414)	1.528(22)	Cl(5) - C(3)	1.753(22)
C(414)-C(415)	1.480(25)	Cl(6) - C(3)	1.717(23)
C(415)-C(416)	1.28(3)	Cl(7) - C(4)	1.79(3)
P(5) -C(501)	1.825(11)	Cl(8) - C(4)	1.33(3)
P(5) -C(507)	1.855(11)	Cl(9) - C(5)	1.69(3)
P(5) -C(513)	1.858(16)	Cl(10)- C(5)	1.38(3)

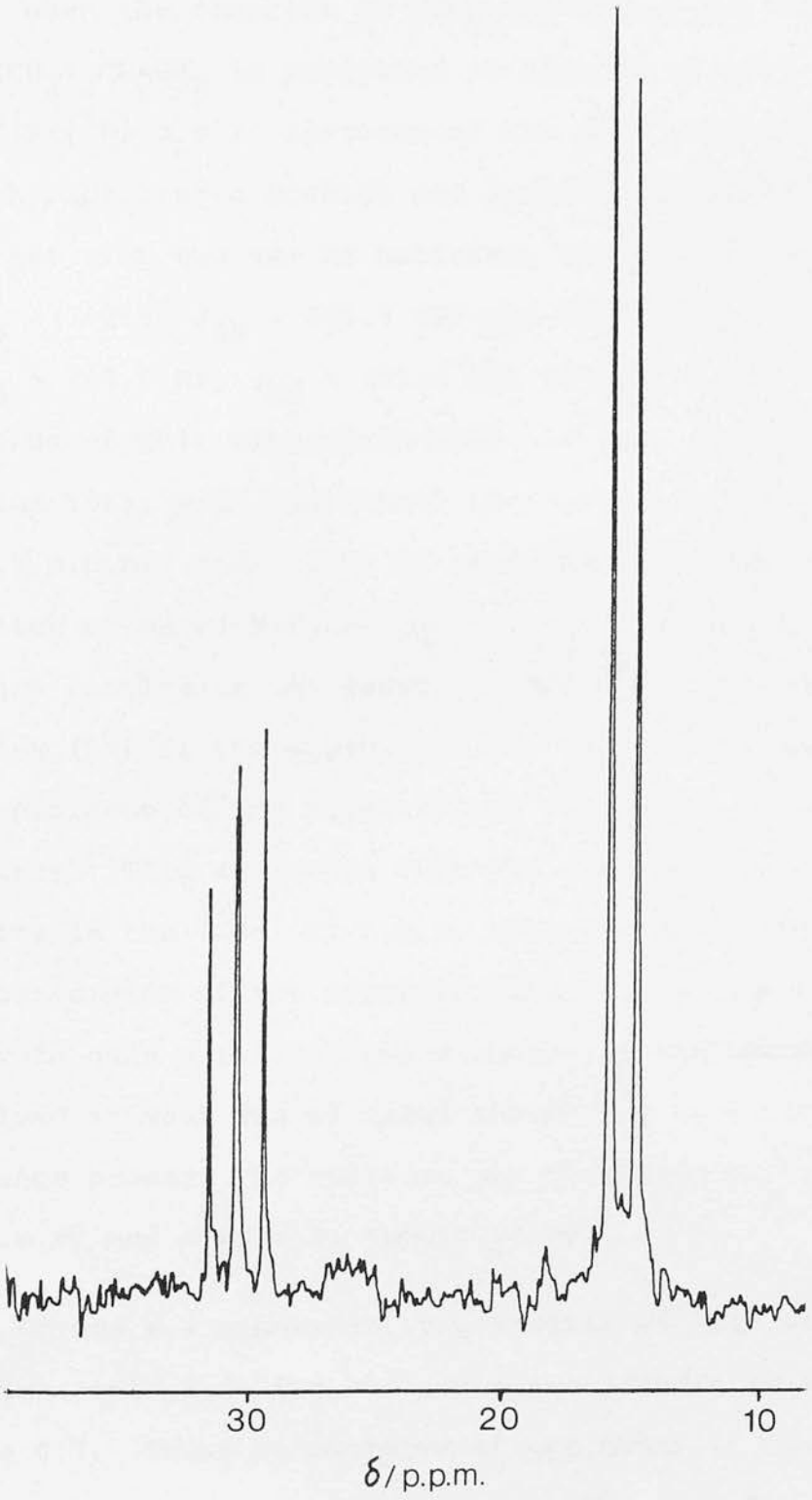
Table 4.5 Bond angles (degrees) with standard deviations for $RuCl_2(CO)(PPh_2(CH_2CH_2CH{=}CH_2))_3$ (56); Molecule 1

Cl(1)	-Ru(1)	-Cl(2)	89.85(14)		
Cl(1)	-Ru(1)	- C(1)	82.7(5)		
Cl(1)	-Ru(1)	- P(1)	81.66(15)		
Cl(1)	-Ru(1)	- P(2)	169.21(15)		
Cl(1)	-Ru(1)	- P(3)	82.09(15)		
Cl(2)	-Ru(1)	- C(1)	172.4(5)		
Cl(2)	-Ru(1)	- P(1)	85.84(14)		
Cl(2)	-Ru(1)	- P(2)	100.91(15)		
Cl(2)	-Ru(1)	- P(3)	85.94(15)		
C(1)	-Ru(1)	- P(1)	91.8(5)		
C(1)	-Ru(1)	- P(2)	86.6(5)		
C(1)	-Ru(1)	- P(3)	94.3(5)		
P(1)	-Ru(1)	- P(2)	99.65(15)		
P(1)	-Ru(1)	- P(3)	161.78(16)		
P(2)	-Ru(1)	- P(3)	97.85(15)		
Ru(1)	- C(1)	- O(1)	177.4(14)		
Ru(1)	- P(1)	-C(101)	122.7(4)		
Ru(1)	- P(1)	-C(107)	112.7(4)		
Ru(1)	- P(1)	-C(113)	110.8(5)		
C(101)	- P(1)	-C(107)	104.2(5)		
C(101)	- P(1)	-C(113)	99.4(6)		
C(107)	- P(1)	-C(113)	105.0(6)		
P(1)	-C(101)	-C(102)	122.5(8)		
P(1)	-C(101)	-C(106)	117.5(8)		
P(1)	-C(107)	-C(108)	119.6(8)		
P(1)	-C(107)	-C(112)	120.4(8)		
P(1)	-C(113)	-C(114)	116.7(11)		
C(113)	-C(114)	-C(115)	111.8(14)		
C(114)	-C(115)	-C(116)	124.9(20)		
Ru(1)	- P(2)	-C(201)	124.8(4)		
Ru(1)	- P(2)	-C(207)	112.5(4)		
Ru(1)	- P(2)	-C(213)	110.4(5)		
C(201)	- P(2)	-C(207)	102.4(5)		
C(201)	- P(2)	-C(213)	103.8(6)		
C(207)	- P(2)	-C(213)	99.9(6)		
P(2)	-C(201)	-C(202)	119.2(8)		
P(2)	-C(201)	-C(206)	120.8(8)		
P(2)	-C(207)	-C(208)	119.4(8)		
P(2)	-C(207)	-C(212)	120.6(8)		
P(2)	-C(213)	-C(214)	120.1(11)		
C(213)	-C(214)	-C(215)	113.1(15)		
C(214)	-C(215)	-C(216)	126.5(20)		
Ru(1)	- P(3)	-C(301)	112.0(4)		
Ru(1)	- P(3)	-C(307)	121.8(4)		
Ru(1)	- P(3)	-C(313)	110.6(5)		
C(301)	- P(3)	-C(307)	105.8(5)		
C(301)	- P(3)	-C(313)	105.3(6)		
C(307)	- P(3)	-C(313)	99.6(6)		
P(3)	-C(301)	-C(302)	120.6(8)		
P(3)	-C(301)	-C(306)	119.4(8)		
P(3)	-C(307)	-C(308)	123.6(8)		
P(3)	-C(307)	-C(312)	116.4(8)		
P(3)	-C(313)	-C(314)	113.2(12)		
C(313)	-C(314)	-C(315)	113.6(17)		
C(314)	-C(315)	-C(316)	127.5(35)		
C(314)	-C(315)	-C(317)	126.4(43)		
C(316)	-C(315)	-C(317)	105.8(50)		

Table 4.6 Bond angles (degrees) with standard deviations for $RuCl_2(CO)(PPh_2(CH_2CH_2CH{=}CH_2))_3$ (56); Molecule 2

Cl(3) -Ru(2) -Cl(4)	89.60(14)	Ru(2) - P(5) -C(513)	109.7(5)
Cl(3) -Ru(2) - C(2)	82.8(5)	C(501)- P(5) -C(507)	102.1(5)
Cl(3) -Ru(2) - P(4)	81.76(15)	C(501)- P(5) -C(513)	103.6(6)
Cl(3) -Ru(2) - P(5)	169.27(15)	C(507)- P(5) -C(513)	100.6(6)
Cl(3) -Ru(2) - P(6)	82.26(15)	P(5) -C(501)-C(502)	119.2(8)
Cl(4) -Ru(2) - C(2)	172.2(5)	P(5) -C(501)-C(506)	120.7(8)
Cl(4) -Ru(2) - P(4)	86.20(14)	P(5) -C(507)-C(508)	120.4(8)
Cl(4) -Ru(2) - P(5)	101.07(15)	P(5) -C(507)-C(512)	119.5(8)
Cl(4) -Ru(2) - P(6)	85.65(15)	C(508)-C(507)-C(512)	120.0(9)
C(2) -Ru(2) - P(4)	91.3(5)	P(5) -C(513)-C(514)	117.5(11)
C(2) -Ru(2) - P(5)	86.6(5)	C(513)-C(514)-C(515)	111.3(15)
C(2) -Ru(2) - P(6)	94.6(5)	C(514)-C(515)-C(516)	127.8(22)
P(4) -Ru(2) - P(5)	99.86(15)	Ru(2) - P(6) -C(601)	121.9(4)
P(4) -Ru(2) - P(6)	162.08(16)	Ru(2) - P(6) -C(607)	112.4(4)
P(5) -Ru(2) - P(6)	97.35(15)	Ru(2) - P(6) -C(613)	111.1(5)
Ru(2) - C(2) - O(2)	177.0(14)	C(601)- P(6) -C(607)	104.5(5)
Ru(2) - P(4) -C(401)	113.1(4)	C(601)- P(6) -C(613)	99.1(6)
Ru(2) - P(4) -C(407)	123.7(4)	C(607)- P(6) -C(613)	106.0(6)
Ru(2) - P(4) -C(413)	110.1(5)	P(6) -C(601)-C(602)	115.5(8)
C(401)- P(4) -C(407)	103.7(5)	P(6) -C(601)-C(606)	124.4(8)
C(401)- P(4) -C(413)	105.0(6)	P(6) -C(607)-C(608)	119.8(8)
C(407)- P(4) -C(413)	99.1(6)	P(6) -C(607)-C(612)	120.0(8)
P(4) -C(401)-C(402)	119.3(8)	P(6) -C(613)-C(614)	113.2(13)
P(4) -C(401)-C(406)	120.7(8)	C(613)-C(614)-C(615)	114.9(18)
P(4) -C(407)-C(408)	117.1(8)	C(614)-C(615)-C(616)	127.8(30)
P(4) -C(407)-C(412)	122.8(8)	C(614)-C(615)-C(616)	123.2(38)
P(4) -C(413)-C(414)	115.2(11)	C(616)-C(615)-C(616)	108.9(43)
C(413)-C(414)-C(415)	111.4(14)	Cl(5) - C(3) -Cl(6)	109.3(12)
C(414)-C(415)-C(416)	127.3(19)	Cl(7) - C(4) -Cl(8)	126.7(18)
Ru(2) - P(5) -C(501)	124.6(4)	Cl(9) - C(5) -Cl(10)	134.2(21)
Ru(2) - P(5) -C(507)	113.3(4)		

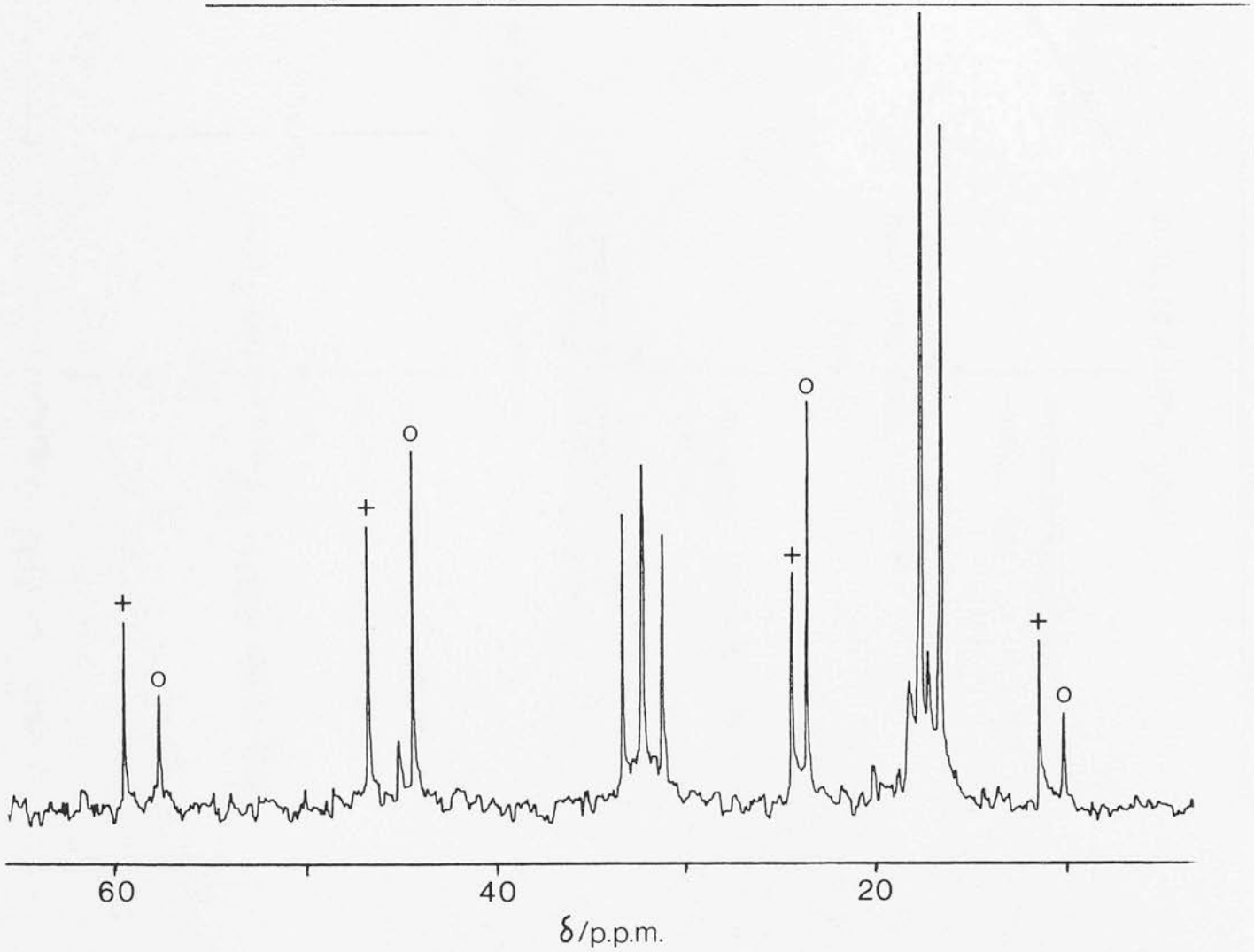
Figure 4.6 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $RuCl_2(CO)(PPh_2(CH_2CH_2CH=CH_2))_3$ (56) in $CDCl_3$



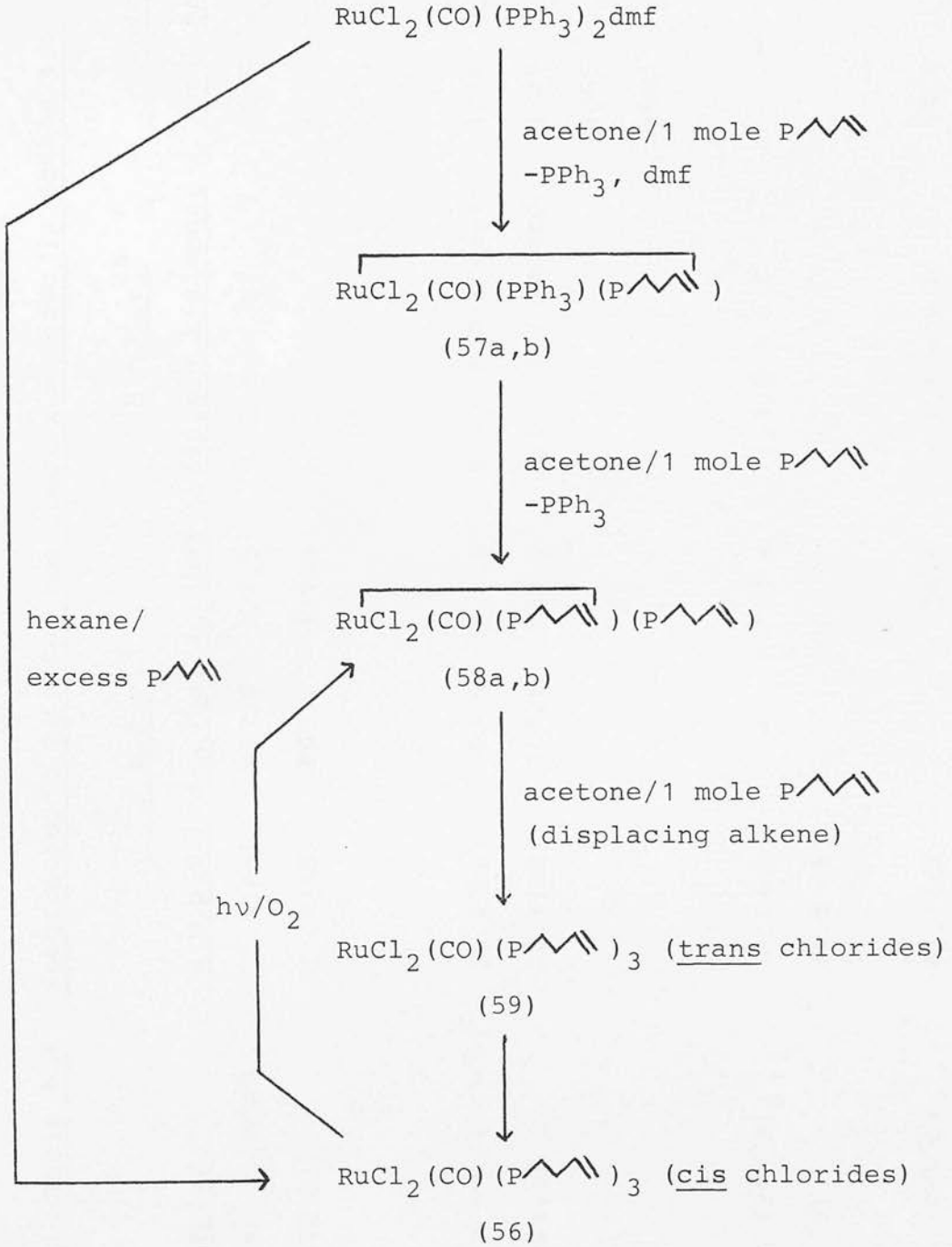
Further study of this reaction was prompted by the outcome of carrying out the reaction in a different solvent. Thus, when the reaction of $RuCl_2(CO)(PPh_3)_2$dmf with $Ph_2P(CH_2)_2CH=CH_2$ is performed in acetone instead of hexane, the $^{31}P-\{^1H\}$ n.m.r. spectrum of the pale yellow product shows the characteristic doublet and triplet of complex (56), together with two new AB patterns, one centred at δ34.4 p.p.m. ($\Delta\nu_{AB}$ = 793.6, J_{AB} = 312.5 Hz) and the other at δ32.9 p.p.m. ($\Delta\nu_{AB}$ = 761.8 Hz, J_{AB} = 323.5 Hz) (Figure 4.7). The ^1H n.m.r. spectrum of this mixture in $CDCl_3$ is very similar to that of complex (56), with additional resonances in the region δ2.5 to 3.7 p.p.m., indicative of coordinated alkene groups. Addition of $Ph_2P(CH_2)_2CH=CH_2$ to a $CDCl_3$ solution of this mixture results in the growth of the ^{31}P n.m.r. signals of complex (56) at the expense of the two AB sets and the disappearance of the bound alkene resonances in the ^1H n.m.r. spectrum. This indicates that the species giving rise to the AB sets in the $^{31}P-\{^1H\}$ n.m.r. spectrum are intermediates in the conversion of the starting material to complex (56). In order to gain a fuller understanding of the sequence of events involved in what was at first thought to be a simple ligand exchange process the reaction was monitored by $^{31}P-\{^1H\}$, ^1H n.m.r. and also i.r. spectroscopy.

Scheme 4.1 summarises the results of this study and the spectroscopic data for the complexes identified are given in Table 4.7. Thus, on addition of <u>one</u> molar equivalent of $Ph_2P(CH_2)_2CH=CH_2$ to a solution of $RuCl_2(CO)(PPh_3)_2$dmf in $CDCl_3$, there is an immediate change in the $^{31}P-\{^1H\}$ n.m.r.

Figure 4.7 $^{31}P-\{^{1}H\}$ n.m.r. spectrum ($CDCl_3$) of the product from reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with excess $Ph_2P(CH_2)_2CH=CH_2$ in acetone



Scheme 4.1 Reaction pathway for reactions of $RuCl_2(CO)(PPh_3)_2dmf$ with $Ph_2P(CH_2)_2CH=CH_2$



P = $Ph_2P(CH_2)_2CH=CH_2$

Table 4.7 Spectroscopic data for the complexes shown in Scheme 4.1

Complex	^{31}P n.m.r.[a] δ(p.p.m.)	$\Delta\nu_{AB}$(Hz)	J_{PP}(Hz)	^{1}H n.m.r.[a] δ(p.p.m.)(alkene)	Infra-red[b] (cm^{-1})	Assignment
$RuCl_2(CO)(PPh_3)(P$$)$[c]	33.8(AB)	877.8	322.3	2.5 - 3.7	1930	$\nu_{C\equiv O}$
	31.7(AB)	800.2	339.4		1950	$\nu_{C\equiv O}$
(57a,b)					1635	$\nu_{C=C}$
$RuCl_2(CO)(P$$)(P$$)$[c]	34.4(AB)	793.6	312,5	4.5 - 6.0 (free)	1930	$\nu_{C\equiv O}$
(58a,b)	32.9(AB)	761.8	323.5	2.5 - 3.7 (coord.)	1950	$\nu_{C\equiv O}$
					1565	$\nu_{C=C}$ (coord.)
					1635	$\nu_{C=C}$ (free)
$RuCl_2(CO)(P$$)_3$[d]	16.7(d)	–	24.4	4.5 - 6.0	–	
(59)	34.8(t)					
$RuCl_2(CO)(P$  $)_3$	16.1(d)	–	24.4	4.5 - 6.0	1958	$\nu_{C\equiv O}$
(56)	31.1(t)				1633	$\nu_{C=C}$
					255	ν_{Ru-Cl}
Continued/					295	ν_{Ru-Cl}

a Recorded in $CDCl_3$ and at ambient temperature (300K)

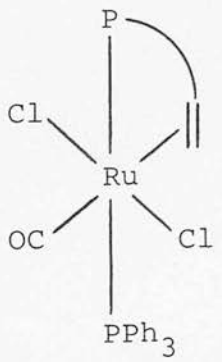
b Nujoll mulls or CH_2Cl_2 solutions

c Not isolated in a pure form

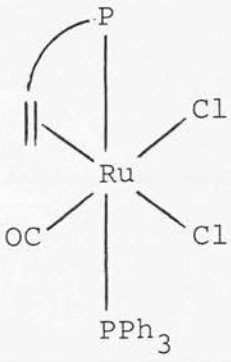
d Not isolated

(d) doublet, (t) triplet

spectrum (Figure 4.8). Two AB patterns are observed, different to those seen in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the product from the reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with an excess of $Ph_2P(CH_2)_2CH=CH_2$ in acetone. The very large coupling constants of these AB sets are consistent with <u>trans</u> arrangements of phosphorus atoms. The ^{1}H n.m.r. spectrum of this solution shows the presence of coordinated alkene groups and its i.r. spectrum contains $\nu_{C\equiv O}$ bands at 1911 cm^{-1} (starting material), 1930 cm^{-1} and 1950 cm^{-1}. Based on this information the species giving rise to the AB sets in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum have been assigned structures (57a) and (57b).



(57a)



(57b)

Complexes (57a) and (57)b are formed in roughly equal amounts and the ratio does not change even after heating solutions containing them for prolonged periods.

On addition of a further molar equivalent of $Ph_2P(CH_2)_2CH=CH_2$ to the above solution the AB patterns shown in Figure 4.7 are seen to grow at the expense of the AB patterns attributed to the complexes (57a) and (57b) (see Figures 4.9 and 4.10). Structures (58a) and (58b) are assigned

Figure 4.8 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $RuCl_2(CO)(PPh_3)_2dmf$ plus $Ph_2P(CH_2)_2CH=CH_2$ (1:1) in $CDCl_3$

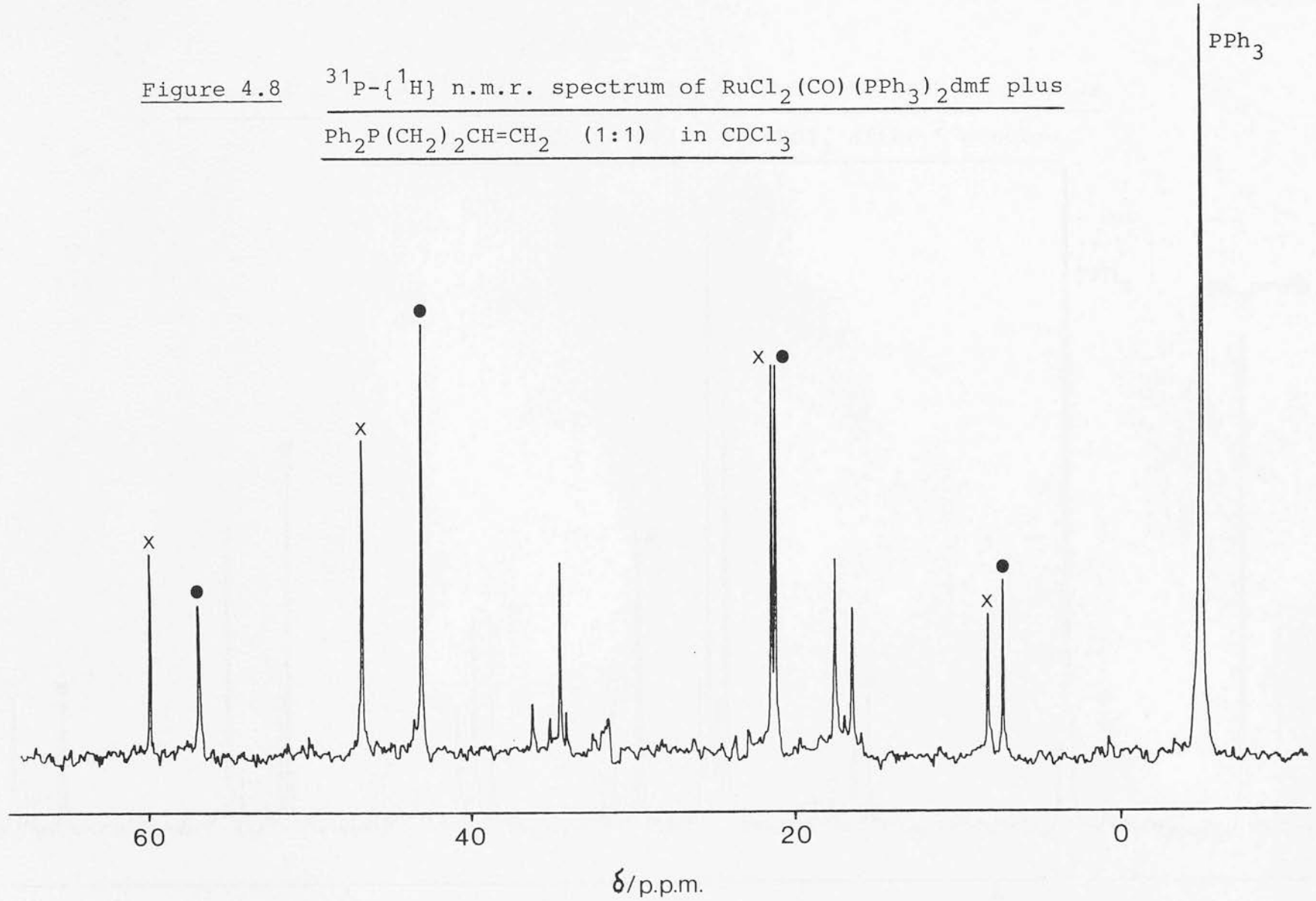


Figure 4.9 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $RuCl_2(CO)(PPh_3)_2$dmf plus $Ph_2P(CH_2)_2CH=CH_2$ (1:2) in $CDCl_3$ after 5 minutes

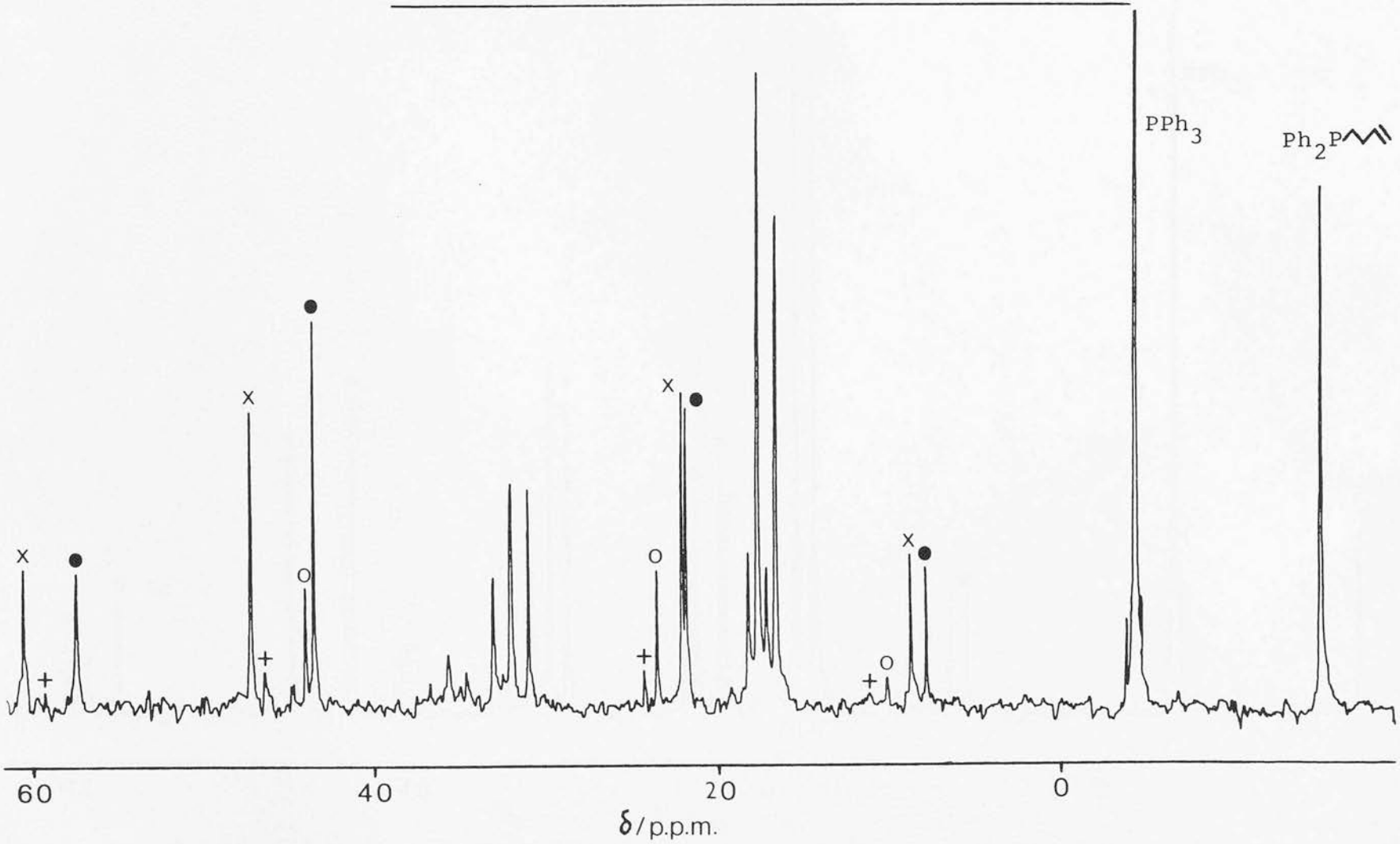
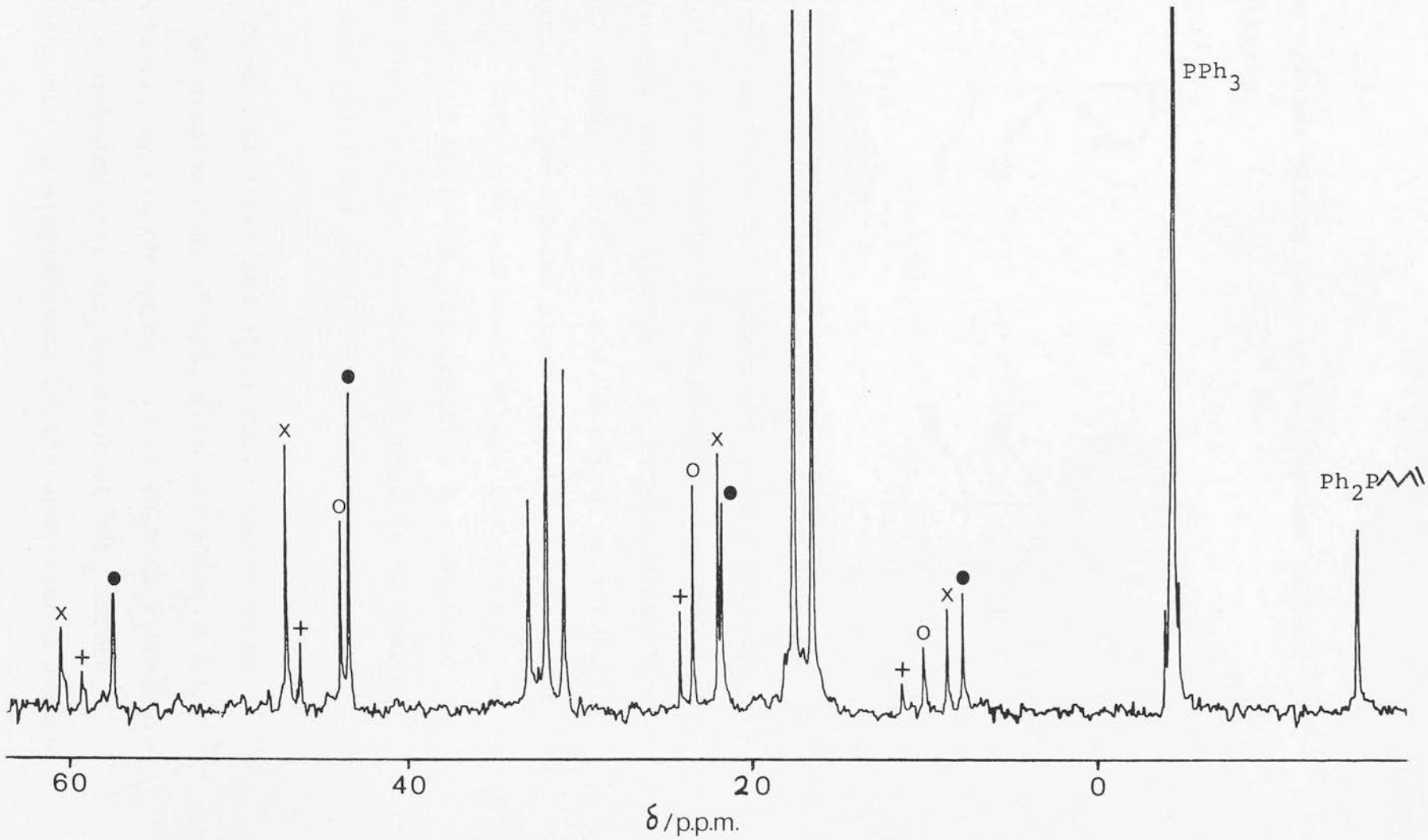
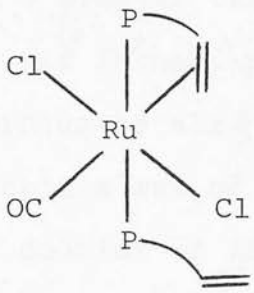


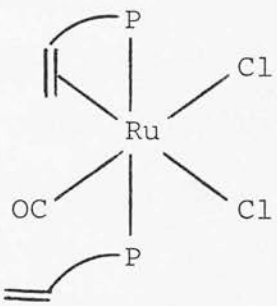
Figure 4.10 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $RuCl_2(CO)(PPh_3)_2dmf$ plus $Ph_2P(CH_2)_2CH=CH_2$ (1:2) in $CDCl_3$ after 25 minutes



to the species giving rise to this second pair of AB patterns.



(58a)



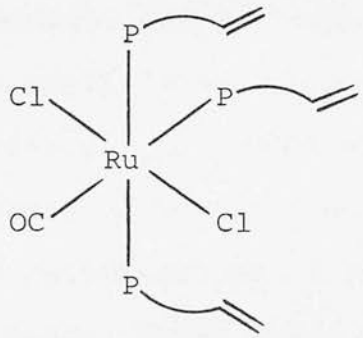
(58b)

The large coupling constants of the ^{31}P n.m.r. AB patterns for these two isomers are thus attributed to the trans arrangements of the phosphorus atoms of one monodentate and one bidentate $Ph_2P(CH_2)_2CH=CH_2$ ligand in each isomer. The ^{1}H n.m.r. spectrum of a solution containing these species alone (see later) shows, as expected, both free and bound alkene resonances. As might also be expected, the solution i.r. spectrum is almost identical (in the carbonyl region) to that of complexes (57a) and (57b).

Complexes (58a) and (58b) would appear to be formed by displacement of PPh_3 from (57a) and (57b) respectively by the phosphine end of $Ph_2P(CH_2)_2CH=CH_2$. It is interesting that displacement of PPh_3 occurs in preference to displacement of the coordinated alkene

group, probably due to a combination of steric constraints and the high stability of the chelate ring.

Even at this stage some $RuCl_2(CO)(PPh_2(CH_2CH_2CH{=}CH_2))_3$ (56) is formed, presumably by displacement of the coordinated alkene groups from (58a) and (58b) by the phosphine end of unreacted $Ph_2P(CH_2)_2CH{=}CH_2$. The triplet and doublet of (56) are seen to grow at the expense of another triplet and doublet with similar chemical shifts and coupling constant. These previously unobserved resonances are attributed to the complex (59), which is an isomer of (56) containing <u>trans</u> chlorides.



(59)

This species is formed by displacement of coordinated alkene from (58a) by the phosphine end of $Ph_2P(CH_2)_2CH{=}CH_2$. It isomerises very quickly to (56), which is known to be the thermodynamically stable form of complexes of general type $RuX_2(CO)(PR_3)_3$ (X = Cl, Br, I).

Adding another molar equivalent of $Ph_2P(CH_2)_2CH=CH_2$ results in complete conversion of all the species in the solution to the complex (56).

All attempts to isolate in a pure form the isomeric pairs (57a,b) and (58a,b), produced by reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with the appropriate amount of $Ph_2P(CH_2)_2CH=CH_2$, have been unsuccessful. The solids obtained were contaminated with starting material and PPh_3 for the pair (57a,b) and with PPh_3 and complex (56) for the pair (58a,b). An alternative route to fairly pure samples of (58a,b) has, however, been found. Thus, complex (56) readily gives crystals from CH_2Cl_2/hexane (as already discussed), and photolysis of a $CDCl_3$ solution of these crystals at 254 nm for 24 hours gives a high yield of (58a,b). On removing the solution from the source of radiation this pair of isomers does not revert to (56) by recombination of dissociated $Ph_2P(CH_2)_2CH=CH_2$ since, under these conditions, the free phosphine is converted to the oxide, as indicated by the appearance of a ^{31}P n.m.r. signal at δ31.0 p.p.m. A poorly soluble off-white solid is deposited as a film on the surface of the photolysis vessel (giving a ^{31}P n.m.r. signal at δ35.0 p.p.m.). This latter material is probably formed by polymerisation of the alkene groups of the free phosphine under the influence of u.v. irradiation. The $^{31}P-\{^1H\}$ n.m.r. spectrum of such a photolysed solution

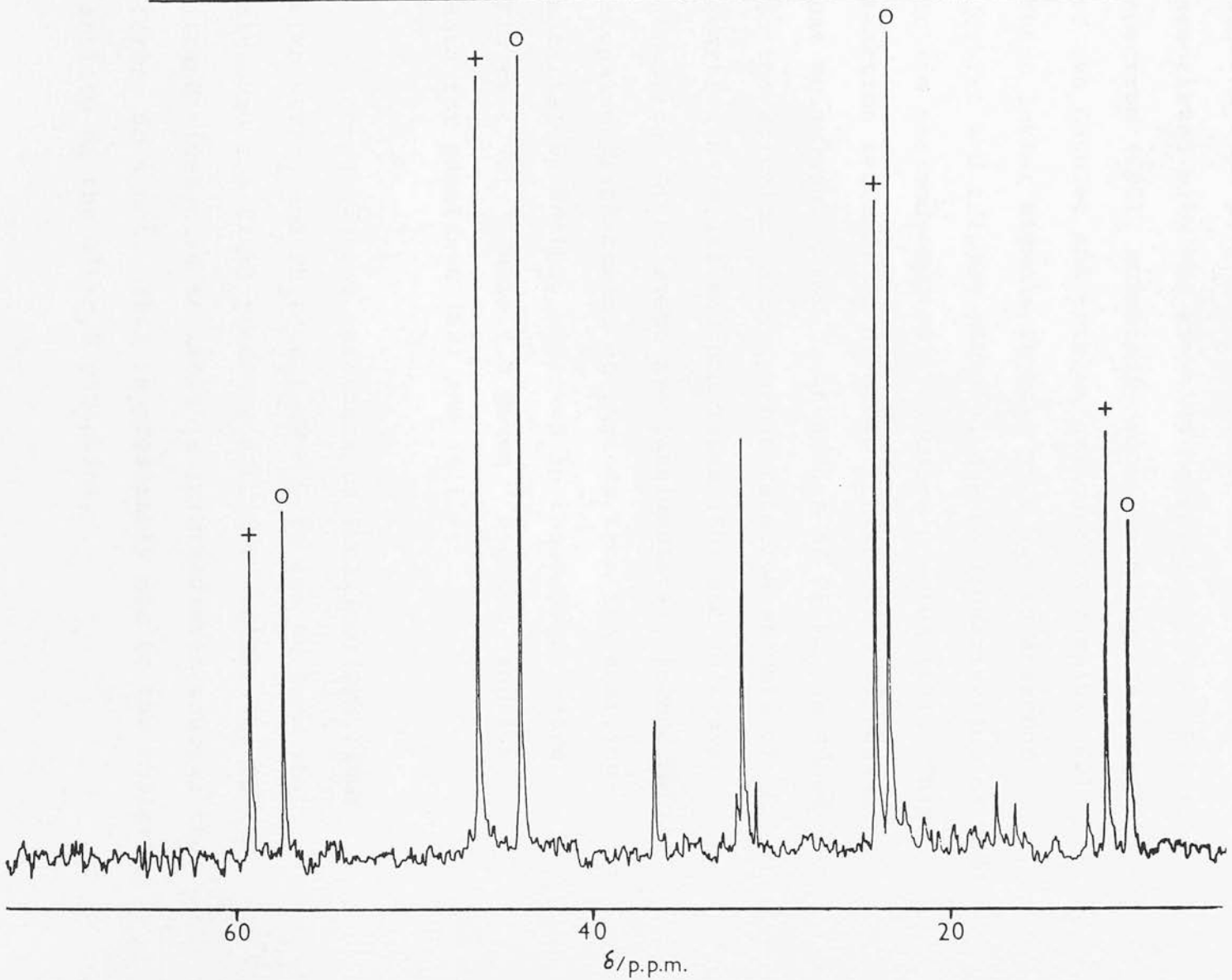
is shown in Figure 4.11. Although samples of (58a,b) prepared in this way are contaminated with the oxide of the alkenyl phosphine, the amount of the contaminant can be lowered considerably by repeated reprecipitation from CH_2Cl_2 or $CHCl_3$ solution on addition of hexane. Note that this synthetic route gives equal amounts of (58a) and (58b), further emphasising the similar stabilities of these two isomers.

The complexes (58a,b) are more soluble in hexane than in acetone which explains why these are obtained along with (56) when $RuCl_2(CO)(PPh_3)_2$dmf is treated with excess $Ph_2P(CH_2)_2CH{=}CH_2$ in acetone. In hexane (58a,b) remain in solution and react further with the excess ligand to give (56) which then precipitates as the sole product.

4.2.2.2 Reaction of $RuCl_2(CO)(PPh_3)_2$dmf with $PEtPh_2$

It is evident from Scheme 4.1 that the bidentate nature of $Ph_2P(CH_2)_2CH{=}CH_2$ and the lability of the resulting coordinated alkene group play a crucial role in the reaction sequence. For comparison, the reaction of $RuCl_2(CO)(PPh_3)_2$dmf with the unidentate tertiary phosphine ethyldiphenylphosphine was examined.

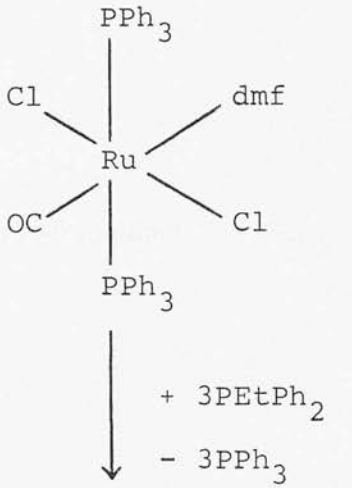
Figure 4.11 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of a $CDCl_3$ solution of $RuCl_2(CO)(PPh_2(CH_2CH_2CH=CH_2))_3$ (56) after irradiation at 254 nm for 24 hours.

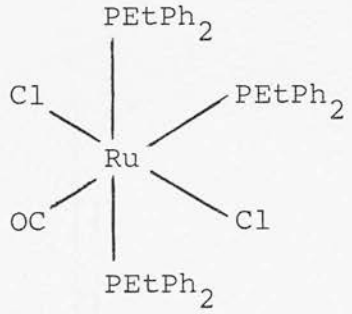


The reaction pathway shown in Scheme 4.2 was deduced from progressive collapse of the singlet associated with the starting material in the ^{31}P n.m.r. spectrum ($CDCl_3$ solution), accompanied by the growth of the doublet and triplet assigned to complex (60). These latter signals rapidly give way to a second doublet and triplet pattern, due to isomerisation of (60) to the thermodynamically favoured complex (61). This reaction sequence is observed irrespective of whether one molar equivalent or an excess of $PEtPh_2$ is added to the solution, although the relative amounts of starting material and complexes (60) and (61) are affected. At no stage are intermediates, formed by the stepwise displacement of ligands from the starting material by $PEtPh_2$, observed in the reaction (see Figure 4.12). Table 4.8 gives ^{31}P n.m.r. and i.r. data for complexes (60) and (61).

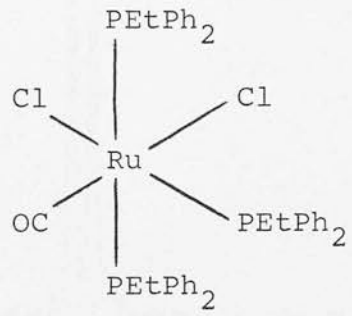
Comparing the reactions of $RuCl_2(CO)(PPh_3)_2dmf$ with $PEtPh_2$ and $Ph_2P(CH_2)_2CH=CH_2$ it can be seen that although the final products are very similar the latter ligand gives rise to isolable intermediates whereas the former does not. This is presumably due to the chelating ability of the alkenyl phosphine.

Scheme 4.2 Reaction pathway for reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with $PEtPh_2$





(60)



(61)

Figure 4.12 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $RuCl_2(CO)(PPh_2)_3dmf$ plus $PEtPh_2$ (1:1) in $CDCl_3$

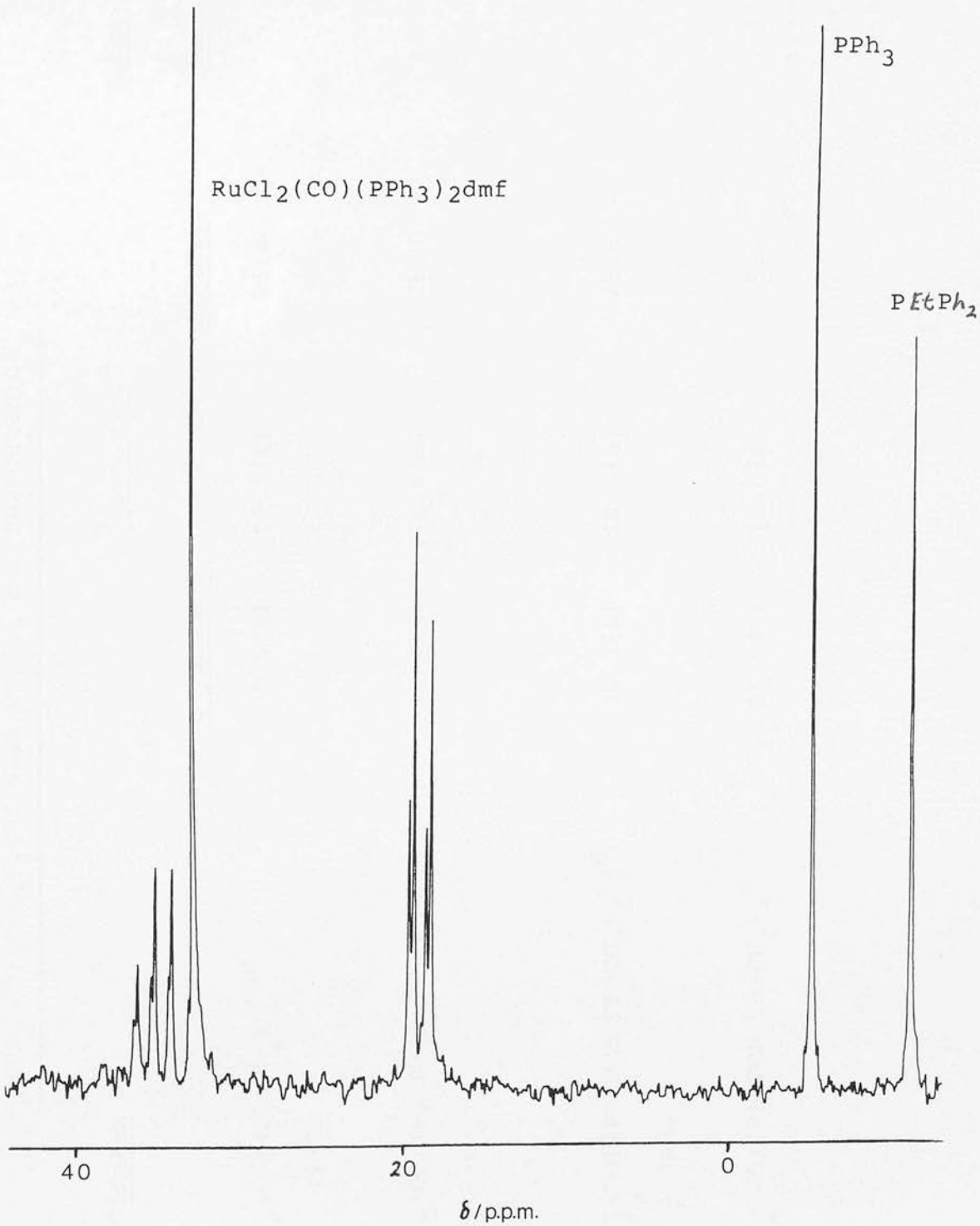


Table 4.8 Spectroscopic data for the complexes formed by reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with $PEtPh_2$ and $Ph_2PCH_2CH=CH_2$

Complex	^{31}P n.m.r.[a]			Infra-red[b]	
	δ (p.p.m.)		J_{PP}(Hz)	cm^{-1}	Assignment
$RuCl_2(CO)(PEtPh_2)_3$[c,d] (60)	35.5(t)	19.1(d)	25.6		
$RuCl_2(CO)(PEtPh_2)_3$[e] (61)	35.3(t)	18.8(d)	25.6	1950	$\nu_{C\equiv O}$
				300	ν_{Ru-Cl}
				250	ν_{Ru-Cl}
$RuCl_2(CO)(Ph_2PCH_2CH=CH_2)_3$[c,d] (63)	35.5(t)	16.3(d)	25.6		
$RuCl_2(CO)(Ph_2PCH_2CH=CH_2)_3$[e]	35.3(t)	16.0(d)	25.6	1950	$\nu_{C\equiv O}$
				1635	$\nu_{C=C}$
				300	ν_{Ru-Cl}
				250	ν_{Ru-Cl}

Table 4.8 (contd.)

[a] Recorded in $CDCl_3$ and at ambient temperature (300 K)

[b] Nujol mull

[c] Not isolated

[d] *trans* chlorides

[e] *cis* chlorides

(d) doublet; (t) triplet

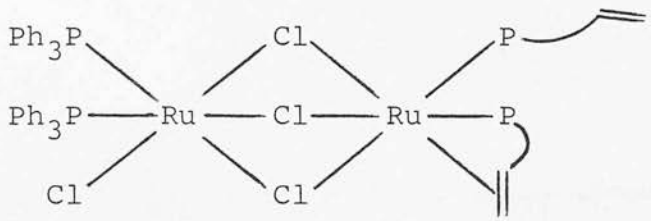
4.2.2.3 Reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with $Ph_2PCH_2CH=CH_2$

A similar reaction sequence to that described above for $PEtPh_2$ is observed with the potentially bidentate ligand $Ph_2PCH_2CH=CH_2$ (allyldiphenylphosphine). The only product isolated is $RuCl_2(CO)(Ph_2PCH_2CH=CH_2)_3$ (62), again as the isomer with cis chlorides. Isomer (63) with trans chlorides is observed in the $^{31}P-\{^1H\}$ n.m.r. spectrum of the reaction solution. Table 4.8 gives the spectroscopic data for these complexes. There is no evidence for intermediates with coordinated alkene groups of the type identified in the reaction with $Ph_2P(CH_2)_2CH=CH_2$. The absence of such intermediates may be attributed to the inability of the $Ph_2PCH_2CH=CH_2$ ligand to bind in a bidentate fashion due to the shorter chain length between the phosphorus atom and the alkene group. A similar contrast in binding mode is exhibited by the previously mentioned complexes $\overline{PtCl_2(Ph_2P(CH_2)_2CH=CH_2)}$ (47) and $PtCl_2(Ph_2PCH_2CH=CH_2)_2$ (49).[116]

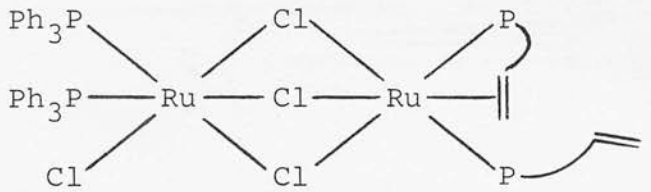
4.3 Coupling Reactions of Monomeric Ruthenium(II) Complexes Containing Alkenyl Phosphines

Reaction of $\overline{RuCl_2(PPh_2(CH_2)CH=CH_2)_2}$ (55) with equimolar $RuCl_2(PPh_3)_3$ in CH_2Cl_2 under reflux gives after work-up a small yield of an orange solid (see experimental methods, section 4.7). The $^{31}P-\{^1H\}$ n.m.r. spectrum of

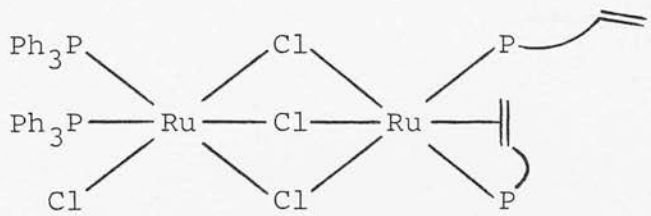
this solid in $CDCl_3$ at ambient temperature (Figure 4.13) is complex, indicating the presence of several species, including the starting materials. Among the many resonances are three pairs of doublets and three superimposed AB patterns (see Table 4.9) which are tentatively assigned to the three isomers of $(Ph_3P)_2ClRuCl_3$-$\overline{Ru(PPh_2(CH_2)_2CH=CH_2)}(PPh_2(CH_2)_2CH=CH_2)$ (64a,b,c).



(64a)



(64b)



(64c)

Thus, there is an AB pattern for the two PPh_3 ligands in each isomer and a pair of doublets for the uni- and bidentate $Ph_2P(CH_2)_2CH=CH_2$ ligands.

Figure 4.13 $^{31}P-\{^{1}H\}$ n.m.r. spectrum ($CDCl_3$) of product from reaction of $RuCl_2(PPh_2(CH_2)CH=CH_2)_2$ (55) and $RuCl_2(PPh_3)_3$

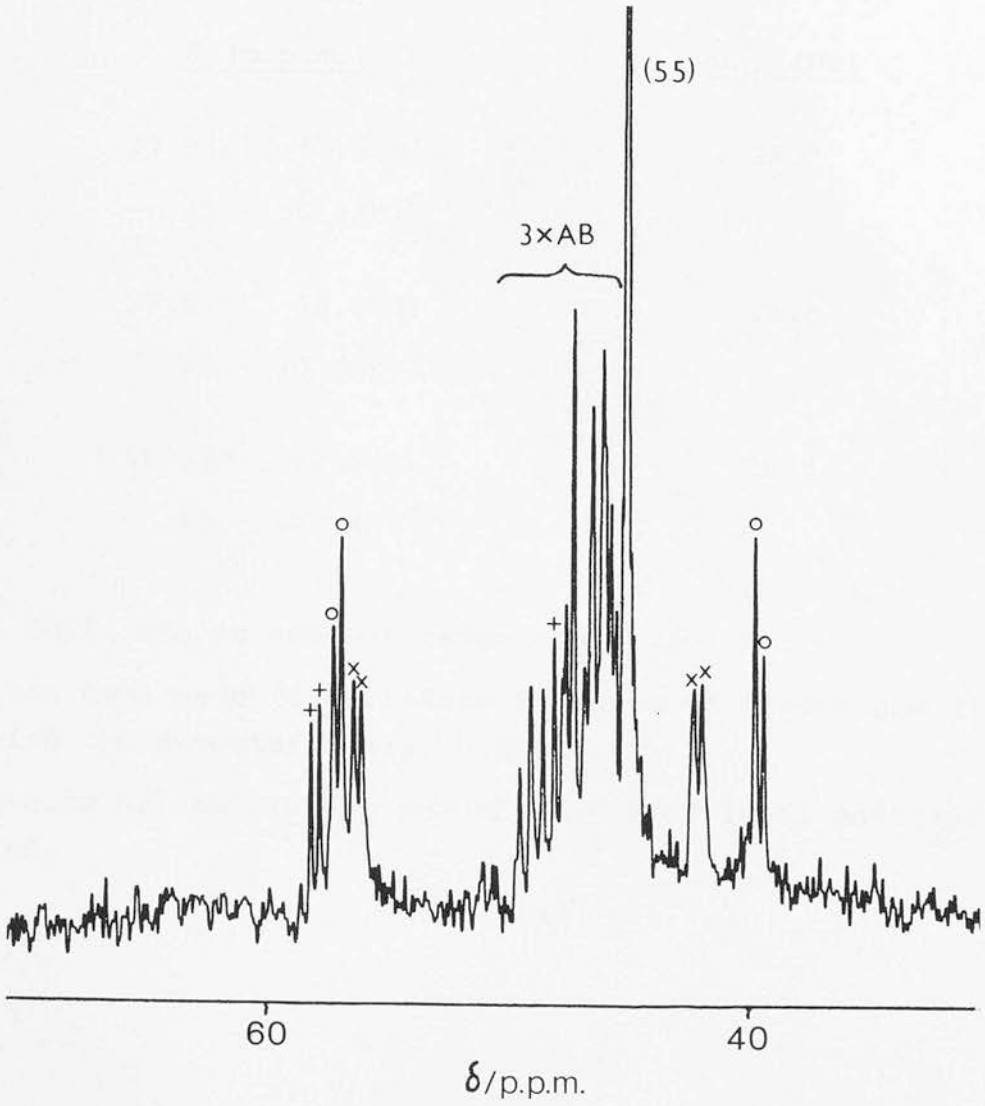


Table 4.9 Tentative $^{31}P-\{^{1}H\}$ n.m.r.[a] assignments for the complex $(Ph_3P)_2ClRuCl_3Ru(PPh_2(CH_2)_2CH=CH_2)(PPh_2(CH_2)CH=CH_2)$ (64)

Isomer[b]	δ (p.p.m.)	J_{PP} (Hz)
(i)	57.9(d), 47.9(d)	29.3
	45 - 50 (AB)[c]	
(ii)	57.0(d), 39.6(d)	28.8
	45 - 50 (AB)[c]	
(iii)	56.2(d), 42.1(d)	26.1
	45 - 50 (AB)[c]	

[a] Recorded in $CDCl_3$ and at ambient temperature (300 K).

[b] No attempt has been made to correlate the sets of resonances (i), (ii) and (iii) with the structures 64a, b and c.

[c] These resonances are so closely spaced that individual patterns cannot be identified.

The mechanism of formation of the postulated isomeric mixture (64a,b,c) is envisaged to be analogous to that proposed for the complex $Ru_2Cl_4(CO)(PPh_3)_4$, formed from $RuCl_2(CO)(PPh_3)_2dmf$ and $RuCl_2(PPh_3)_3$[4a,d] (see Chapter 1, Section 1.4.1). Thus, dissociation of an alkene group from $\overline{RuCl_2(PPh_2(CH_2)_2CH=CH_2)_2}$ may give a five-coordinate intermediate which can then couple with $RuCl_2(PPh_3)_3$ with loss of PPh_3 to give the three triple-chloride-bridged isomers.

Attempts to increase the yields of the three isomers (64a,b,c) by increasing the reflux time (greater than 3 hours) for the reaction of $\overline{RuCl_2(PPh_2(CH_2)_2CH=CH_2)_2}$ with $RuCl_2(PPh_3)_3$ in CH_2Cl_2 have been unsuccessful, the products obtained being even more complex mixtures than that already described. Similarly, carrying out the reaction in a more polar solvent such as acetone gives products with extremely complicated ^{31}P n.m.r. spectra. All attempts to separate these various mixtures have been unsuccessful.

The poor yield of (64a,b,c) is probably due to the high stability of $\overline{RuCl_2(PPh_2(CH_2)_2CH=CH_2)_2}$ (55), making formation of the five-coordinate species,which is required for the coupling reaction, unfavourable. For the same reason (55) has not been found to undergo self-coupling reactions (cf. $RuCl_2(CO)(PPh_3)_2dmf$,

which readily gives rise to a five-coordinate species and forms various $Ru_2Cl_4(CO)_2(PPh_3)_3$ compounds under relatively mild conditions[4a,d].

The reactions between the complexes $\overline{RuCl_2(CO)(Ph_2P(CH_2)_2CH=CH_2)}(PPh_3)$ (57a,b) or $\overline{RuCl_2(CO)(Ph_2P(CH_2)_2CH=CH_2)}(Ph_2P(CH_2)_2CH=CH_2)$ (58a,b) and $RuCl_2(PPh_3)_3$ in CH_2Cl_2 or acetone also give extremely complicated and, to date, inseparable mixtures.

In view of the complexity of the product mixtures obtained in these reactions, this approach to preparing triple-chloride-bridged complexes containing alkenyl phosphines *via* coupling of monomer precursors was not pursued.

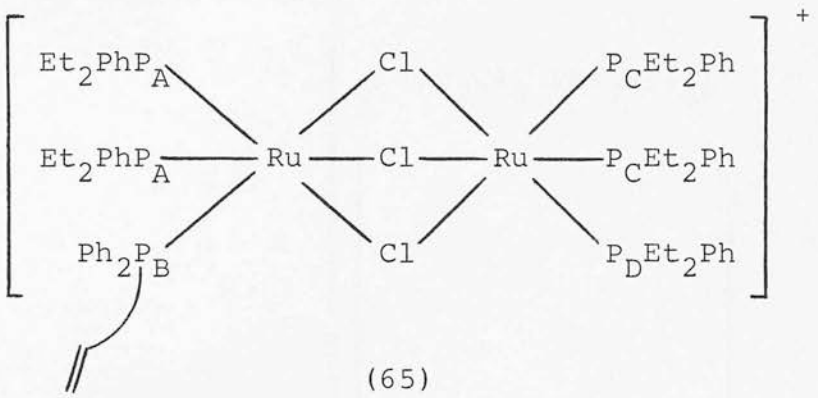
4.4 Incorporation of Alkenyl Phosphines into Binuclear Triple-Chloride-Bridged Ruthenium(II) Complexes by Terminal Chloride Abstraction

This section describes work which follows on directly from that described in Chapter 2. It was shown there that $TlBF_4$ is an extremely effective terminal chloride abstracting agent and, in the presence of suitable ligands L, complexes of the type $[Ru_2Cl_3(L)(PEt_2Ph)_5]BF_4$ can be prepared in high yield (L = C_2H_4, N_2, PEt_2Ph, *etc.*).

It therefore appears likely that alkenyl phosphines may be introduced in the same way with the possibility that they may bind in a bidentate fashion through displacement of a PEt_2Ph ligand.

Thus, treatment of a CH_2Cl_2 solution of the orange complex $Ru_2Cl_4(PEt_2Ph)_5$ with equimolar amounts of $TlBF_4$ and $Ph_2P(CH_2)_2CH{=}CH_2$ gives a yellow solution. Filtering off the precipitate of TlCl and removing the solvent from the filtrate gives a yellow oil which, on trituration with n-hexane gives a yellow powder. Analysis figures for this product are consistent with the formulation $[Ru_2Cl_3(Ph_2P(CH_2)_2CH{=}CH_2)(PEt_2Ph)_5]BF_4$. The i.r. spectrum indicates a free alkene group ($\nu_{C=C}$ at 1630 cm^{-1}), and an intense broad band at 1025 cm^{-1} is attributed to the presence of BF_4^-. Retention of the triple-chloride-bridged structure is indicated by ν_{Ru-Cl} at 240 cm^{-1}. This is the only ν_{Ru-Cl} band observed which is good evidence for the successful abstraction of terminal chloride. The ^1H n.m.r. spectrum of this complex is very similar to that of the starting complex except for the presence of a group of resonances in the region δ4.7 to 6.0 p.p.m. corresponding to the protons of a non-coordinated alkene group. Integration values are consistent with one free alkene group per binuclear unit.

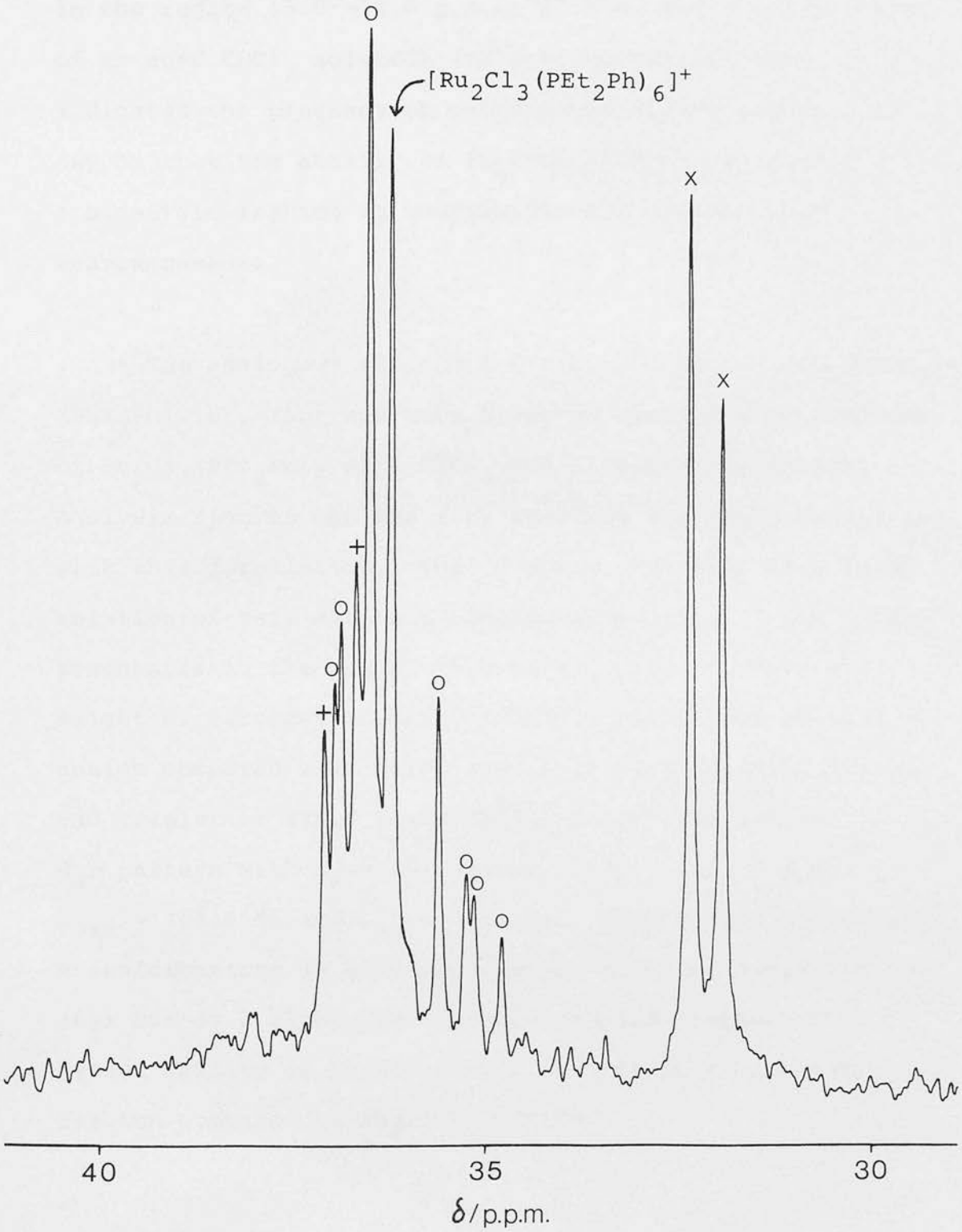
Assignment of structure (65) to this complex is supported by the $^{31}P-\{^{1}H\}$ n.m.r. spectrum in $CDCl_3$ at room temperature.



(65)

The spectrum (Figure 4.14) consists of a doublet centred at δ32.2 p.p.m. and triplet at δ36.7 p.p.m. ($^{2}J_{PP}$ = 33.2 Hz) corresponding to the two P_A and one P_B nuclei, respectively. An A_2B pattern is observed for the two P_C and one P_D nuclei ($\delta_A(P_C)$ = 36.7 p.p.m.; $\delta_B(P_D)$ = 35.3 p.p.m.; $\Delta\nu_{AB}$ = 115.4 Hz; J_{AB} = 34.2 Hz). The peak at δ36.2 p.p.m. is due to the cation $[Ru_2Cl_3(PEt_2Ph)_6]^+$ which is present in very small quantities in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of a freshly prepared solution of (65) but steadily increases with time. After several hours at ambient temperature the neutral complex $Ru_2Cl_4(PEt_2Ph)_5$ is also formed in this solution as indicated by a singlet at δ44.0 p.p.m. and an AB_2 pattern at δ35.0 p.p.m. (which is masked to a large extent by the other resonances in that region). The mechanism of formation of these latter two

Figure 4.14 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[Ru_2Cl_3(Ph_2P(CH_2)_2CH=CH_2)(PEt_2Ph)_5]BF_4$ (65) in $CDCl_3$



compounds is not known at the time of writing but may involve bridge cleavage of (65) to give monomers which then undergo coupling reactions. A group of resonances in the region δ3.0 - 4.0 p.p.m. of the ^1H n.m.r. spectrum of an aged $CDCl_3$ solution (several hours) of (65) indicates the presence of coordinated alkene groups. It may be that the ability of $Ph_2P(CH_2)_2CH=CH_2$ to bind in a bidentate fashion is responsible for the observed rearrangements.

The analogous binuclear cation $[Ru_2Cl_3(PH_2PCH_2CH=CH_2)-(PEt_2Ph)_5]BF_4$ (66) has been prepared similarly by reaction of $Ru_2Cl_4(PEt_2Ph)_5$ with $TlBF_4$ and allyldiphenylphosphine. Analysis figures and the i.r. spectrum are again consistent with this formulation. The ^1H n.m.r. spectrum of a fresh solution of this cationic complex shows free alkene group resonances in the region δ4.5 to 6.0 p.p.m. There are slight differences in the ^{31}P n.m.r. parameters of this cation compared with (65), i.e. a doublet at δ31.3 p.p.m. and triplet at δ36.7 p.p.m. ($^2J_{PP}$ = 33.7 Hz) and an A_2B pattern with δ_A = 36.6 p.p.m.; δ_B = 35.3 p.p.m.; $\Delta\nu_{AB}$ = 106.6 Hz and J_{AB} = 34.5 Hz. This cation undergoes transformations in solution similar to those exhibited by (65) but at a slower rate, which probably reflects the lesser ability of $Ph_2PCH_2CH=CH_2$ to bind in a bidentate fashion compared to $Ph_2P(CH_2)_2CH=CH_2$.

Because of the facile rearrangements which the cations (65) and (66) undergo in solution, no attempt has been made to study the reactions of these species with nucleophiles.

4.5 Conclusions

The monomeric complexes $RuCl_2(PPh_3)_3$ and $RuCl_2(CO)(PPh_3)_2$dmf have been shown to readily undergo ligand displacement reactions with but-4-enyldiphenylphosphine, the final products of which have been fully characterised by spectroscopic methods and also by X-ray structural analysis. In the case of $RuCl_2(CO)(PPh_3)_2$dmf the ligand displacement proceeds in a series of discrete steps and the intermediates involved have been isolated (in an impure state) and characterised. Similar reactions with allyldiphenylphosphine and ethyldiphenylphosphine do not exhibit such a variety of intermediates although the final products are identical in the arrangement of ligands about the metal. The difference in the reaction pathways is attributed to the ability of but-4-enyldiphenylphosphine to bind to the metal via both the phosphorus atom and the alkene group.

Attempted coupling reactions between monomeric ruthenium complexes containing alkenyl phosphines and $RuCl_2(PPh_3)_3$ have met with limited success. In all

cases the products consisted of inseparable mixtures of species, some of which have been tentatively identified by spectroscopic analysis.

Terminal chloride abstraction from $Ru_2Cl_4(PEt_2Ph)_5$ in the presence of but-4-enyldiphenylphosphine gives the cationic complex $[Ru_2Cl_3(Ph_2P(CH_2)_2CH=CH_2)(PEt_2Ph)_5]^+$. This species and its allyldiphenylphosphine analogue were found to rearrange in solution to give mixtures of species, these rearrangements probably being facilitated by the tendency of the alkenyl phosphine to bind to the metal in a bidentate fashion.

The ultimate aim of the work presented in this chapter was to study the reactivity towards nucleophiles of metal-bound alkene groups of alkenyl phosphines in triple-chloride-bridged ruthenium complexes. This has not been achieved because of the difficulty encountered in synthesising such complexes in high yield and in a pure form. The tendency of some of these complexes to rearrange in solution presented another problem. Despite this, some interesting and unexpected chemistry has been discovered. Of particular note is the fascinating fluctuation between PPh_2R ($R = (CH_2)_2CH=CH_2$) displacing PPh_3, alkene displacing dmf, and PPh_2R displacing chelated alkene in the reaction of $RuCl_2(CO)(PPh_3)_2$dmf with PPh_2R.

The following chapter describes a short series of experiments which was prompted by these observations.

4.6 Experimental Methods

Physical measurements were performed as described in Chapter 2.

Materials

The following were prepared using literature methods: $RuCl_2(PPh_3)_3$,[119] $RuCl_2(CO)(PPh_3)_2dmf$[120] and $Ru_2Cl_4(PEt_2Ph)_5$.[7b] The alkenyl phosphines $Ph_2PCH_2CH{=}CH_2$ and $Ph_2P(CH_2)_2CH{=}CH_2$ were provided by New Science Group of Imperial Chemical Industries, plc.

Dichlorobis(but-4-enyldiphenylphosphine)ruthenium(II), $RuCl_2(Ph_2P(CH_2)_2CH{=}CH_2)_2$ (55)

$RuCl_2(PPh_3)_3$ (0.68 g, 0.7 mmol) and $Ph_2P(CH_2)_2CH{=}CH_2$ (1.02 g, 4.3 mmol) were heated in degassed n-hexane (50 cm^3) under N_2 for 30 minutes. The mustard coloured precipitate was washed with n-hexane. The solid was warmed in a small amount of CH_2Cl_2 and the solution filtered to remove a small quantity of sticky green material. Yellow crystals of the product were deposited from the filtrate on addition of excess MeOH, m.p. 212(d) (0.32 g; 69%).

Found: C, 58.7; H, 5.2. Calc. for $C_{32}H_{34}Cl_2P_2Ru$: C, 58.9; H, 5.2%.

Mull i.r. spectrum: $\nu_{C=C}$ 1565(w), ν_{Ru-Cl} 280, 325(m) cm^{-1}.

Dichlorocarbonyl(but-4-enyldiphenylphosphine)-(triphenylphosphine)ruthenium(II), $RuCl_2(CO)(Ph_2P(CH_2)_2CH=CH_2)(PPh_3)$ (57a,b)

$RuCl_2(CO)(PPh_3)_2$dmf (0.20 g, 0.25 mmol) and $Ph_2P(CH_2)_2CH=CH_2$ (0.06 g, 0.25 mmol) were stirred in degassed acetone (50 cm^3) under N_2 for 2 hours. The solvent was removed *in vacuo* and the pale yellow oil triturated with n-hexane to give an off-white powder. $^{31}P-\{^1H\}$ n.m.r. studies showed that this solid contained, apart from (57a,b), a small amount of starting material, PPh_3 and $OPPh_3$.

i.r. spectrum in $CDCl_3$: $\nu_{C\equiv O}$ 1911(m), 1930(s), 1950(s) cm^{-1}.

Dichlorocarbonylbis(but-4-enyldiphenylphosphine)-ruthenium(II), $RuCl_2(CO)(Ph_2P(CH_2)_2CH=CH_2)(Ph_2P(CH_2)_2CH=CH_2)$ (58a,b)

Method (1): $RuCl_2(CO)(PPh_3)_2$dmf (0.20 g, 0.25 mmol) and $Ph_2P(CH_2)_2CH=CH_2$ (0.12 g, 0.50 mmol) were stirred in degassed acetone (50 cm^3) under N_2 for 2 hours. The solution was worked up as for (57a,b) above to give a very pale yellow solid. $^{31}P-\{^1H\}$ n.m.r. studies showed that this solid was contaminated with a small amount of complex (56), PPh_3 and $OPPh_3$.

i.r. spectrum in $CDCl_3$: $\nu_{C\equiv O}$ 1930(s), 1950(s), 1960(m), $\nu_{C=C}$ 1635(w), 1560(w) cm^{-1}.

Method (2): $RuCl_2(CO)(Ph_2P(CH_2)_2CH=CH_2)_3$ (56) (0.20 g, 0.22 mmol) was dissolved in CH_2Cl_2 (2 cm^3) and irradiated at 254 nm for 24 hours in a quartz n.m.r. tube. The pale yellow solution was concentrated to a sticky oil in vacuo and a small amount of n-hexane added. The off-white precipitate was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to contain a small amount of the oxide of the alkenyl phosphine, which could be lowered by repeated reprecipitation from CH_2Cl_2/n-hexane but never removed completely. m.p. 150(d) (0.10 g, 68%).

Found: C, 60.1; H, 5.4. Calc. for $C_{33}H_{34}Cl_2OP_2Ru$: C, 58.2; H, 5.0%.

i.r. spectrum in $CDCl_3$: $\nu_{C\equiv O}$ 1930(s), 1950(s), $\nu_{C=C}$ 1635(w), 1565(w) cm^{-1}.

Dichlorocarbonyltris(but-4-enyldiphenylphosphine)-ruthenium(II), $RuCl_2(CO)(Ph_2P(CH_2)_2CH=CH_2)_3$ (56)

$RuCl_2(CO)(PPh_3)_2dmf$ (0.20 g, 0.25 mmol) and $Ph_2P(CH_2)_2CH=CH_2$ (0.36 g, 1.50 mmol) were heated in degassed n-hexane (50 cm^3) under N_2 for 2 hours. The pale yellow precipitate was dissolved in a small amount of CH_2Cl_2 and an excess of hexane added to give yellow crystals of the product. m.p. 195(d) (0.13 g, 56.5%).

Found: C, 64.0; H, 5.5. Calc. for $C_{49}H_{51}Cl_2OP_3Ru$: C, 63.9; H, 5.5%.

Mull i.r. spectrum: $\nu_{C\equiv O}$ 1958(s), $\nu_{C=C}$ 1633(w), ν_{Ru-Cl} 295,255(w) cm^{-1}.

Dichlorocarbonyltris(allyldiphenylphosphine)-ruthenium(II), $RuCl_2(CO)(Ph_2PCH_2CH=CH_2)_3$ (62)

This complex was prepared in the same way as (56) above using $RuCl_2(CO)(PPh_3)_2dmf$ (0.20 g, 0.25 mmol) and $Ph_2PCH_2CH=CH_2$ (0.34 g, 1.50 mmol). m.p. 170(d), (0.17 g, 77.3%).

Found: C, 62.7; H, 5.0. Calc. for $C_{46}H_{45}Cl_2OP_3Ru$: C, 62.9; H, 5.1%.

Mull i.r. spectrum: $\nu_{C\equiv O}$ 1950(s), $\nu_{C=C}$ 1635(w), ν_{Ru-Cl} 300, 250(w) cm^{-1}.

Dichlorocarbonyltris(ethyldiphenylphosphine)ruthenium(II), $RuCl_2(CO)(PEtPh_2)_3$ (61)

This complex was prepared in the same way as (56) and (62) above, using $RuCl_2(CO)(PPh_3)_2dmf$ (0.20 g, 0.25 mmol) and $PEtPh_2$ (0.32 g, 1.50 mmol). m.p. 205(d) (0.15 g, 71.3%).

Found: C, 61.4; H, 5.3. Calc. for $C_{43}H_{45}Cl_2OP_3Ru$: C, 61.3; H, 5.3%.

Mull i.r. spectrum: $\nu_{C\equiv O}$ 1950(s), ν_{Ru-Cl} 300, 250(w) cm^{-1}.

Reaction between $RuCl_2(Ph_2P(CH_2)_2CH=CH_2)_2$ (55) and $RuCl_2(PPh_3)_3$

$RuCl_2(Ph_2P(CH_2)_2CH=CH_2)_2$ (0.07 g, 0.11 mmol) and $RuCl_2(PPh_3)_3$ (0.10 g, 0.11 mmol) were heated in degassed CH_2Cl_2 (50 cm^3) under N_2 for 3 hours. The reddish-brown solution was concentrated *in vacuo* and an excess of petroleum ether (b.p. 60-80°C) added. A small amount of unreacted $RuCl_2(PPh_3)_3$ deposited and was filtered off. On reducing the volume of the filtrate *in vacuo*, a light orange precipitate formed. This was filtered off and washed with petroleum ether (b.p. 40-60°C) (yield 0.07 g). This solid was a mixture of species and is discussed fully in the main text.

def-Tri-μ-chloro-a-(but-4-enyldiphenylphosphine)-bcghi-pentakis(diethylphenylphosphine)diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(Ph_2P(CH_2)_2CH=CH_2)(PEt_2Ph)_5]BF_4$ (65)

$Ru_2Cl_4(PEt_2Ph)_5$ (0.10 g, 0.09 mmol), $TlBF_4$ (0.03 g, 0.11 mmol) and $Ph_2P(CH_2)_2CH=CH_2$ (0.02 g, 0.09 mmol) were stirred in degassed CH_2Cl_2 (25 cm^3) under argon for 2 hours. The white precipitate of TlCl was filtered off from the yellow solution. The solvent was removed from the filtrate *in vacuo* and the yellow oil triturated with n-hexane to give a yellow powder. m.p. 140-143°C (0.12 g, 96%).

Found: C, 53.8; H, 6.2. Calc. for $C_{66}H_{92}BCl_3F_4P_6Ru_2$: C, 54.0; H, 6.3%.

Mull i.r. spectrum: $\nu_{C=C}$ 1630(w), BF_4^- 1025(s,br), ν_{Ru-Cl} 240(w) cm^{-1}.

This compound may also be prepared by treatment of $[Ru_2Cl_3(N_2)(PEt_2Ph)_5]BF_4$ or $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ with equimolar quantities of $Ph_2P(CH_2)_2CH=CH_2$.

def-Tri-μ-chloro-a-(allyldiphenylphosphine)-bcghi-pentakis(diethylphenylphosphine)diruthenium(II) tetrafluoroborate, $[Ru_2Cl_3(Ph_2PCH_2CH=CH_2)(PEt_2Ph)_5]BF_4$ (66)

This compound was prepared as for (65) above, using $Ru_2Cl_4(PEt_2Ph)_5$ (0.10 g, 0.09 mmol), $TlBF_4$ (0.03 g, 0.11 mmol) and $Ph_2PCH_2CH=CH_2$ (0.02 g, 0.09 mmol). m.p. 148-152°C (0.11 g, 90%).

Found: C, 53.5; H, 6.2. Calc. for $C_{65}H_{90}BCl_3F_4P_6Ru_2$: C, 53.7; H, 6.2%.

Mull i.r. spectrum: $\nu_{C=C}$ 1630(w), BF_4^- 1025(s,br), ν_{Ru-Cl} 240(w) cm^{-1}.

CHAPTER 5

REACTIONS OF $RuCl_2(CO)(PPh_3)_2$)dmf

WITH ALKYNES

Chapter 5

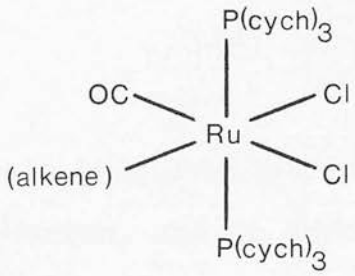
Reactions of $RuCl_2(CO)(PPh_3)_2dmf$ with Alkynes

5.1 Introduction

In the previous chapter the stepwise reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with $Ph_2P(CH_2)_2CH=CH_2$ was discussed. If the incorporation of the first molecule of the alkenyl phosphine proceeded alkene-first via displacement of the labile dmf ligand from the starting complex then it follows that the same substrate may react with "simple" alkenes and alkynes.

The five-coordinate species $RuCl_2(CO)(PPh_3)_2$ has been found to be surprisingly inactive towards the hydrogenation of alkenes but is an active catalyst for alkene isomerisation.[121] Indeed, it may be the catalytic intermediate formed in the isomerisation of alkenes in the presence of $RuCl_2(PPh_3)_3$ and hydroperoxides, from which system complexes of the type $RuCl_2(CO)_2(PPh_3)_2$ and $RuCl_2(CO)(alkene)(PPh_3)_2$ were isolated.[122] Note that the nature of the alkene is not specified but is described as C_8H_{12}, which in the context of the paper concerned may be inferred to be either cis or trans 4-ethylidene-cyclohexene. The related five-coordinate species $RuCl_2(CO)(P(cych)_3)_2$ has been isolated both from the mother liquor from the

preparation of $RuHCl(CO)(P(cych)_3)_2$ and by treatment with $P(cych)_3$ of the red solution obtained from passing CO into "$RuCl_3.xH_2O$" in 2-methoxyethanol at 80°C.[123] It reacts with various cyanoalkenes to give $RuCl_2(CO)(alkene)(P(cych)_3)_2$ (67) or, with tcne to give $(RuCl_2(CO)(P(cych)_3)_2)_2tcne$.[23]

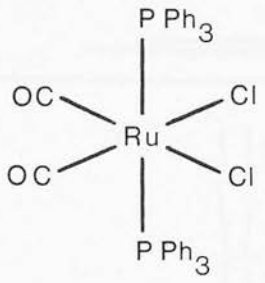


(67)

The following discussion is concerned with experiments which explore the possibility of preparing alkyne or alkene complexes from $RuCl_2(CO)(PPh_3)_2dmf$.

5.2 The Reaction with Phenylacetylene

On treating the yellow complex $RuCl_2(CO)(PPh_3)_2dmf$ with an excess of phenylacetylene (1:6 molar ratio) in $CHCl_3$ or CH_2Cl_2 and stirring at room temperature for 4 hours, a white product can be isolated in quantitative yield. This complex has been identified by conventional methods as the well-known dicarbonyl complex $RuCl_2(CO)_2(PPh_3)_2$ with cis carbonyl ligands, cis chlorides and trans PPh_3 ligands (68).[121]

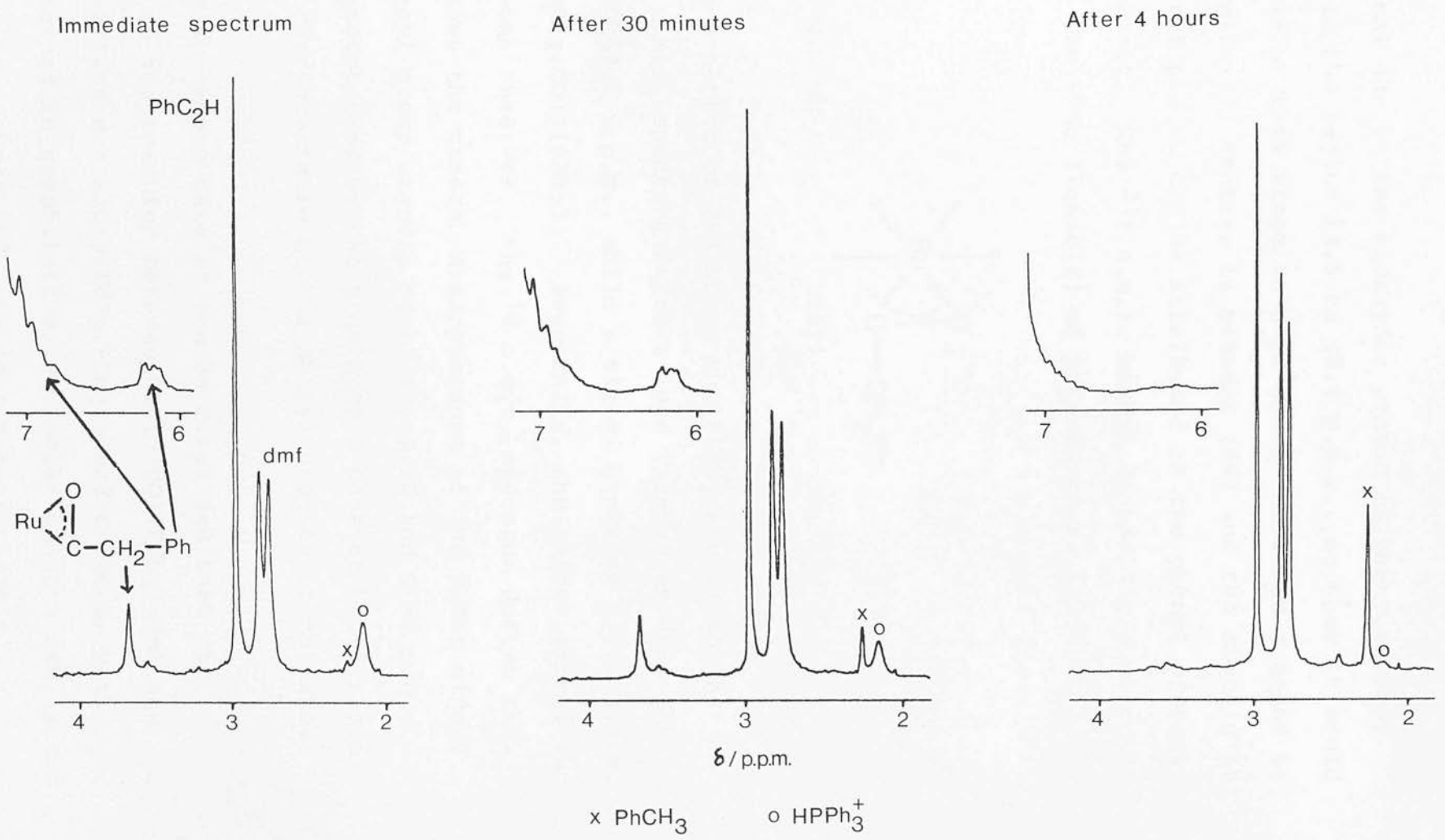


(68)

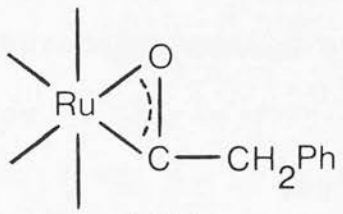
In order to gain some insight into the mechanism of this unexpected reaction, and to ascertain the role and ultimate fate of the phenylacetylene, the reaction has been monitored by $^{31}P-[^{1}H]$ and ^{1}H n.m.r. spectroscopy.

Within minutes of adding a six-fold excess of phenylacetylene to a solution of $RuCl_2(CO)(PPh_3)_2dmf$ in $CDCl_3$ at ambient temperature a peak in the $^{31}P-[^{1}H]$ n.m.r. spectrum at δ20.8 p.p.m. (due to $HPPh_3^+$) grows at the expense of the peak due to the starting material (δ34.1 p.p.m.). An additional peak is observed at δ41.1 p.p.m. The ^{1}H n.m.r. spectrum at this stage (Figure 5.1) shows a broad peak at δ2.15 p.p.m. attributed to the phosphorus-bound proton of $HPPh_3^+$ and a singlet at δ3.67 p.p.m., as well as signals due to free phenylacetylene and dmf. There are also a complex set of phenyl resonances in the region δ7.0 to 8.0 p.p.m. and small, broad resonances centred at δ6.2 and 6.9 p.p.m. The peak at δ3.67 p.p.m. is typical of the protons of a methylene group attached to both a carbonyl moiety and a phenyl ring, as in phenylacetaldehyde. There is no evidence

Figure 5.1 ^1H n.m.r. spectrum of $RuCl_2(CO)(PPh_3)_2dmf$ plus phenylacetylene (1:6) in $CDCl_3$



for a signal due to the aldehydic proton of phenylacetaldehyde in the region δ9.5 to 10.0 p.p.m., so that it would appear that at this stage an acyl group, presumably bound to the ruthenium(II) centre, is present (69) and the signals at δ6.2 and 6.9 p.p.m. can be attributed to the phenyl protons of this moiety. The ^{31}P n.m.r. signal at δ41.1 p.p.m. could be due to the PPh_3 ligand(s) of this species.



(69)

Over a period of 2-3 hours the $HPPh_3^+$ signal in the $^{31}P-[^1H]$ n.m.r. spectrum becomes less intense as does the signal at δ41.1 p.p.m., while a signal grows at δ17.2 p.p.m. due to $RuCl_2(CO)_2(PPh_3)_2$. Eventually, the latter signal is the only one observed. The ^1H n.m.r. spectrum during this period shows the gradual disappearance of the $HPPh_3^+$ signal and the acyl group signals at δ3.67, 6.20 and 6.90 p.p.m. This is accompanied by the growth of a peak at δ2.25 p.p.m. which is characteristic of the methyl protons of toluene.

From the above data it can be concluded that the products of the reaction between $RuCl_2(CO)(PPh_3)_2$dmf and phenylacetylene are $RuCl_2(CO)_2(PPh_3)_2$ and toluene, both being obtained in quantitative, equimolar amounts (the yield of toluene was determined from ^1H n.m.r. integrals).

The source of the oxygen in the additional carbonyl ligand of (68) is most likely to be traces of water in the solvent since the reaction in dry $CDCl_3$ follows a different, and as yet unresolved, course.

Cleavage of the triple bond in terminal alkynes by the monomeric ruthenium(II) complex $[RuCl(bipy)_2(H_2O)]^+$ in aqueous solution has been reported and involves a metal-promoted hydration/disproportionation of the alkyne (Equation 5.1).[124]

$$\underline{cis}\text{-}[RuCl(bipy)_2(H_2O)]^+ + PhC{\equiv}CH \xrightarrow[H_2O]{100\,^\circ C} \underline{cis}\text{-}[RuCl(bipy)_2(CO)]^+ + PhCH_3 \qquad (5.1)$$

With the diaqua cations $\underline{cis}$-$[Ru(bipy)_2(H_2O)_2]^{2+}$ and cis-$[Ru(terpy)(PPh_3)(H_2O)_2]^{2+}$ ruthenium-carbonylbenzyl complexes are formed (Equation 5.2).

$$\underline{cis}\text{-}[Ru(bipy)_2(H_2O)_2]^{2+} + 2PhC{\equiv}CH \xrightarrow[H_2O]{100\,^\circ C} \underline{cis}\text{-}[Ru(bipy)_2(CO)(\eta\text{-}CH_2Ph)]^+ + PhCH_3 + CO + H^+ \qquad (5.2)$$

The incorporation of H and O atoms from water in the carbonylbenzyl product was shown by i.r. spectroscopy using $H_2{}^{18}O$ where $\nu_{C=}{}^{16}{}_O$ = 1944 cm^{-1} and $\nu_{C=}{}^{18}{}_O$ = 1896 cm^{-1} in the product and by ^1H n.m.r. using D_2O where the disappearance of benzylic proton resonances was observed. The mechanisms for the conversion of phenylacetylene to CO and toluene or to CO and the benzyl complex were not known but postulated

intermediates included ethyne, vinylidene, acetylide, hydroxycarbene and acyl complexes, all of which have precedents in the chemistries of Re(I), Pt(II), Ru(II) and Fe(II).

The similarity between the reactions of these monomeric ruthenium(II) species with phenylacetylene and the reaction described here is evident. The latter, however, has the advantage of taking place at ambient temperature so that it can be easily monitored by the methods already described. This has allowed the observation of what is most probably an acyl complex as one of the intermediates. Additional experiments have provided further information on the mechanism involved. The appearance of $HPPh_3^+$ and the known acidity of terminal alkynes[125] suggests that the first stage is the formation of an acetylide complex, which then reacts with trace amounts of water to form an acyl complex by addition of the water across the carbon-carbon triple bond. This acyl complex may then rearrange with cleavage of a carbon-carbon bond to give a dicarbonylbenzyl complex which reacts further with the $HPPh_3^+$ present in solution to give toluene and the dicarbonyl complex (68). In an attempt to observe an acetylide complex $RuCl_2(CO)(PPh_3)_2$dmf was treated with phenylacetylene in dry $CDCl_3$ in the presence of "proton sponge" (1,8-bis-(dimethylamino)naphthalene) so that the postulated reactions with water and proton could not occur. The $^{31}P-[^1H]$ n.m.r. spectrum of this solution showed a very rapid loss of the peak at δ 34.1 p.p.m. due to starting material and the appearance of a peak at δ 37.5 p.p.m., possibly due to the acetylide complex. As expected, no

$HPPh_3^+$ is observed (due to the presence of "proton sponge"). It should be noted that there is no apparent reaction between PPh_3 and phenylacetylene or between $RuCl_2(CO)(PPh_3)_2dmf$ and "proton sponge". On addition of a small amount of water to the solution of the acetylide species, the $^{31}P-[^1H]$ n.m.r. spectrum shows the growth of a resonance at δ41.0 p.p.m. at the expense of the peak at δ37.5 p.p.m. and this is attributed to the acyl complex formed by attack of water on the acetylide complex. In addition some free PPh_3 and $OPPh_3$ are observed at this stage perhaps indicating that the water is first coordinated to the metal centre by displacement of one of the PPh_3 ligands, thus facilitating its attack on the acetylide group. On standing for several minutes the $^{31}P-[^1H]$ n.m.r. spectrum of this solution shows the growth of a new peak at δ36.0 p.p.m. which could be a dicarbonylbenzyl complex formed by rearrangement of the acyl complex. Unfortunately confirmation of the presence of such a complex by ^1H n.m.r. spectroscopy is not possible due to the presence of the "proton sponge" which gives a very complicated, poorly resolved spectrum, masking the areas where the benzylic protons might be expected to occur. If dilute HCl is added to the solution containing the postulated benzyl complex there is a rapid reaction to give the dicarbonyl complex (68) as the only species detectable by ^{31}P n.m.r. spectroscopy. Presumably toluene is also formed although

this could not be confirmed by ^1H n.m.r. spectroscopy for this particular solution for the reason already mentioned.

Scheme 5.1 summarises the pathway postulated for this reaction. It has not been possible to isolate the various intermediates proposed, all of them being insufficiently stable.

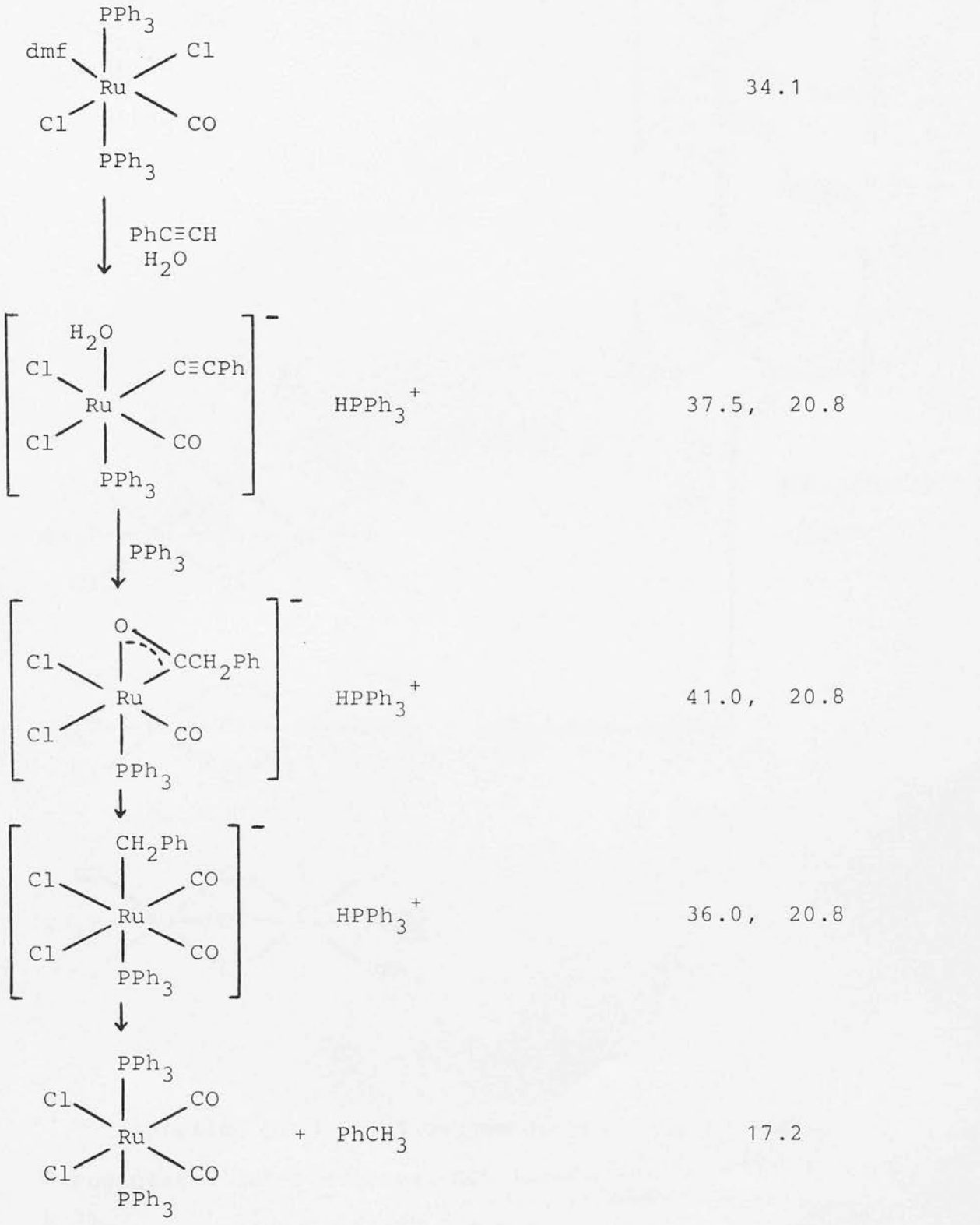
5.3 The Reaction with dimethylacetylenedicarboxylate

Having studied in some detail the reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with phenylacetylene attention turned to the reaction with an alkyne bearing no terminal ≡C-H function. Such an alkyne is dimethylacetylenedicarboxylate ($MeO_2CC{\equiv}CCO_2Me$, dmac).

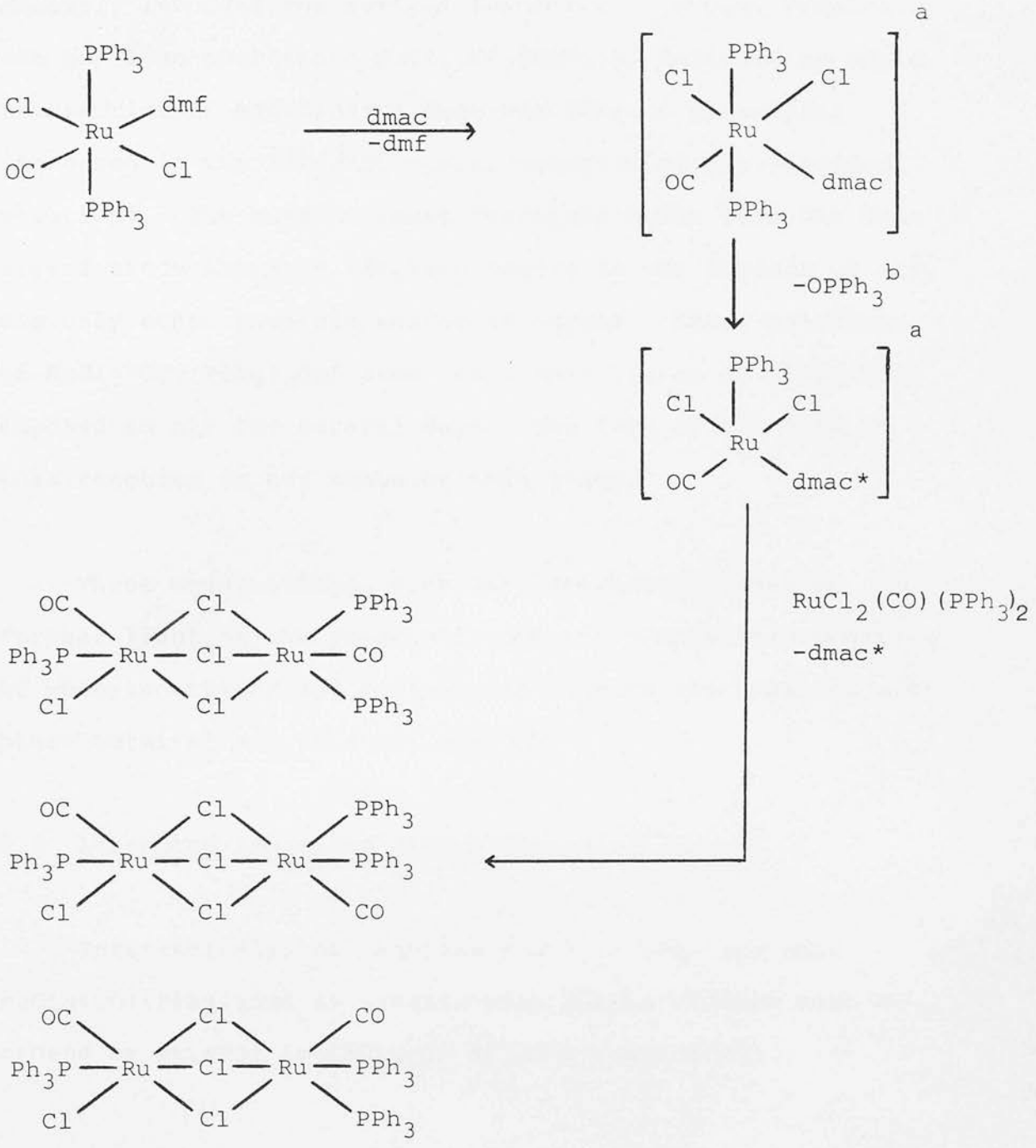
To cut a long story short, dmac is susceptible to O-donation to PPh_3 leading to an interesting and efficient route to the known di-carbonyl binuclear complex $Ru_2Cl_4(CO)_2(PPh_3)_3$ in its three isomeric forms (see Scheme 5.2).

This complex has been prepared previously by reaction of $RuCl_2(CO)(PPh_3)_2MeOH$ in warm CH_2Cl_2/light petroleum (bp 60-80°C)[4a] and by treatment of the complexes $RuHCl(CO)(PPh_3)_3$[80] and $RuH_2(CO)(PPh_3)_3$[79] with gaseous HCl. The mechanism proposed for these reactions involves the formation of the five-coordinate intermediate

Scheme 5.1 Possible pathway for the reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with phenylacetylene



Scheme 5.2 Possible pathway for the reaction of $RuCl_2(CO)(PPh_3)_2dmf$ with dmac



* Unidentified product of oxygen abstraction from dmac.

[a] Postulated intermediates, not observed.

[b] ^{31}P n.m.r. signal at δ29.0 p.p.m.

$RuCl_2(CO)(PPh_3)_2$ and subsequent intermolecular coupling with loss of PPh_3 to give the product. The reaction between $RuCl_2(CO)(PPh_3)_2$dmf and dmac to give the same complex probably involves the initial formation of a dmac complex via the five-coordinate $RuCl_2(CO)(PPh_3)_2$, followed by rapid interaction of coordinated dmac and PPh_3 to give $OPPh_3$ (detected in the $^{31}P-[^1H]$ n.m.r. spectrum of the reaction solution). The oxygen almost certainly comes from the dmac ligand since the same reaction occurs in the absence of air, the only other possible source of oxygen. Also, solutions of $RuCl_2(CO)(PPh_3)_2$dmf alone show only traces of $OPPh_3$ when exposed to air for several days. The fate of the dmac in this reaction is not known at this stage.

These observations, although interesting, shed no further light on the remarkable ambient temperature reaction of phenylacetylene and further experiments are required with other terminal and internal alkynes.

5.4 Attempted Reactions with Alkenes

Interestingly, no reaction has been observed when $RuCl_2(CO)(PPh_3)_2$dmf is treated with simple alkenes such as ethene or styrene in $CDCl_3$ at ambient temperature.

5.5 Conclusions

The experiments described in this chapter suggest that simple alkyne and alkene complexes cannot readily be prepared from $RuCl_2(CO)(PPh_3)_2dmf$. It would appear that the reactions with phenylacetylene and dmac are "special cases". With respect to the former cleavage of the triple bond in terminal alkynes by monomeric ruthenium complexes has been observed previously but in this case the mild conditions used allow *in situ* study of the reaction and a tentative mechanism has been proposed.

5.6 Experimental Methods

Physical measurements were performed as described in Chapter 2.

Materials

The complex $RuCl_2(CO)(PPh_3)_2dmf$ was prepared as described in the literature.[120] Phenylacetylene, dimethylacetylenedicarboxylate, styrene, "proton sponge" (BDH) and ethene (Matheson) were used as received.

The reaction between $RuCl_2(CO)(PPh_3)_2dmf$ and phenylacetylene

$RuCl_2(CO)(PPh_3)_2dmf$ (0.10 g, 0.12 mmol) and phenylacetylene (0.07 g, 0.7 mmol) were stirred in degassed CH_2Cl_2 (5 cm^3) under N_2 for 4 hours. The solvent was removed from the pale yellow solution in vacuo and the yellow oil triturated with n-hexane to give a white powder which was washed with n-hexane to remove excess phenylacetylene. Recrystallisation from CH_2Cl_2/hexane gave white needles of $RuCl_2(CO)_2(PPh_3)_2$.(68) mp 239-242°C (0.09 g, 95%).

Found: C, 60.4; H, 3.9. Calc. for $C_{38}H_{30}Cl_2O_2P_2$: C, 60.6; H, 4.0%.

Mull ir spectrum: $\nu_{C\equiv O}$ 2050, 1990(s), ν_{Ru-Cl} 300, 275 (m) cm^{-1}.

The reaction between $RuCl_2(CO)(PPh_3)_2dmf$ and dimethylacetylenedicarboxylate (dmac)

$RuCl_2(CO)(PPh_3)_2dmf$ (0.10 g, 0.12 mmol) and dmac (0.10 g, 0.70 mmol) were shaken in degassed CH_2Cl_2 (5 cm^3) under N_2 for 24 hours to give an orange crystalline product which consisted of the three isomers of $Ru_2Cl_4(CO)_2(PPh_3)_3$. This was filtered off and washed with n-hexane. The filtrate gave more product on being allowed to slowly evaporate. mp 245-248°C (0.06 g, 84%).

Found: C, 56.9; H, 3.9. Calc. for $C_{56}H_{45}Cl_4O_2P_3Ru_2$: C, 56.6; H, 3.8%.

Mull i.r. spectrum: $\nu_{C\equiv O}$ 1960 (s,br), ν_{Ru-Cl} 310, 250 (m) cm^{-1}.

CHAPTER 6

REACTIONS OF MONOMERIC AND BINUCLEAR RUTHENIUM(II) COMPLEXES WITH SILVER(I) COMPOUNDS.

Chapter 6

Reactions of Monomeric and Binuclear Ruthenium(II) Complexes with Silver(I) Compounds

6.1 Introduction

The initial aim of the work presented in this chapter was to synthesise fluoride-bridged binuclear ruthenium(II) complexes analogous to the chloride complexes used extensively in Chapters 2 and 3. Such complexes would be of great interest in themselves, and could be useful starting materials with which to carry out terminal fluoride abstraction reactions in the presence of alkenes, alkynes etc.

Complexes of ruthenium(II) which contain both tertiary phosphine and fluoride ligands are scarce in comparison to the vast number of chloride species which have been prepared. To a large extent this may be due to the unavailability of a fluoride analogue of "commercial" ruthenium(III) chloride, the main starting material for the chloride complexes. Ruthenium(III) fluoride is available as a dark brown powder but is of limited synthetic use because of its insolubility in most solvents.

Some of the ruthenium(II) tertiary phosphine/fluoride complexes which have been prepared are the products of somewhat unusual reactions, the species isolated not being those expected. For example, reaction of trans-$RuCl_2(dppe)_2$ with $AgBF_4$ under an atmosphere of CO produces a mixture of two complexes, one of which is the expected trans-$[Ru(CO)_2(dppe)_2](BF_4)_2$. The other is $[RuF(CO)(dppe)_2]BF_4$, which is believed to be formed via an ion paired intermediate, $Ru(BF_4)Cl(dppe)_2$.[126]

The only reported example of a binuclear triple-fluoride-bridged ruthenium(II) species is the cation $[(Me_2PhP)_3RuF_3Ru(PMe_2Ph)_3]^+$, prepared by reaction of $[RuH(cod)(NH_2NMe_2)_3]PF_6$ with PMe_2Ph and HF in refluxing acetone-methanol.[127]

A synthetic route which has been used to prepare fluoride complexes of several transition metals is typified by the treatment of $RuCl(\eta\text{-}C_5H_5)(PPh_3)_2$ with NH_4F in refluxing methanol followed by addition of Ag_2CO_3 to give $RuF(\eta\text{-}C_5H_5)(PPh_3)_2$.[128] This method, abstraction of Cl^- by Ag(I) in the presence of a large excess of F^-, has been investigated in the present work. Although it has failed to provide new ruthenium(II) phosphine/fluoride complexes, these conditions have resulted in the isolation of some unexpected and unusual fluoride-free complexes. Of particular interest is the mixed

Ru/Ag compound $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$, initially made by treatment of $RuCl_2(PEtPh_2)_3$ with Ag_2CO_3 and HF but subsequently shown to form by a rational synthetic pathway involving simply $Ru_2Cl_4(PEt_2Ph)_5$ and AgCl.

Further attempts to obtain the desired fluoride complexes are described towards the end of this chapter.

6.2.1 Reactions of $RuCl_2(PEtPh_2)_3$, $Ru_2Cl_4(PEtPh_2)_5$ and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ with AgCl and $Ag(PEtPh_2)_2Cl$

Reaction of $RuCl_2(PEtPh_2)_3$ with AgCl in methanol at ambient temperature gives a red-brown solid which on recrystallisation from CH_2Cl_2/MeOH yields red crystals of the CH_2Cl_2 solvate of the novel heterotrimetallic complex $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ (70). A single crystal X-ray analysis has been carried out on this complex and the structure is shown in Figure 6.1. Selected bond lengths and bond angles are given in Tables 6.1 and 6.2 respectively.

The structure consists of a four-coordinate silver(I) ion linked to one terminal and two bridging chloride ligands of the newly formed $[(EtPh_2P)_2ClRuCl_3RuCl(PEtPh_2)_2]^-$ unit. Comparison of the bond lengths and angles of this unit with those for related binuclear structures show that it is little affected by the presence of the $Ag(PEtPh_2)^+$ group.

Figure 6.1 The structure of $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ (70).

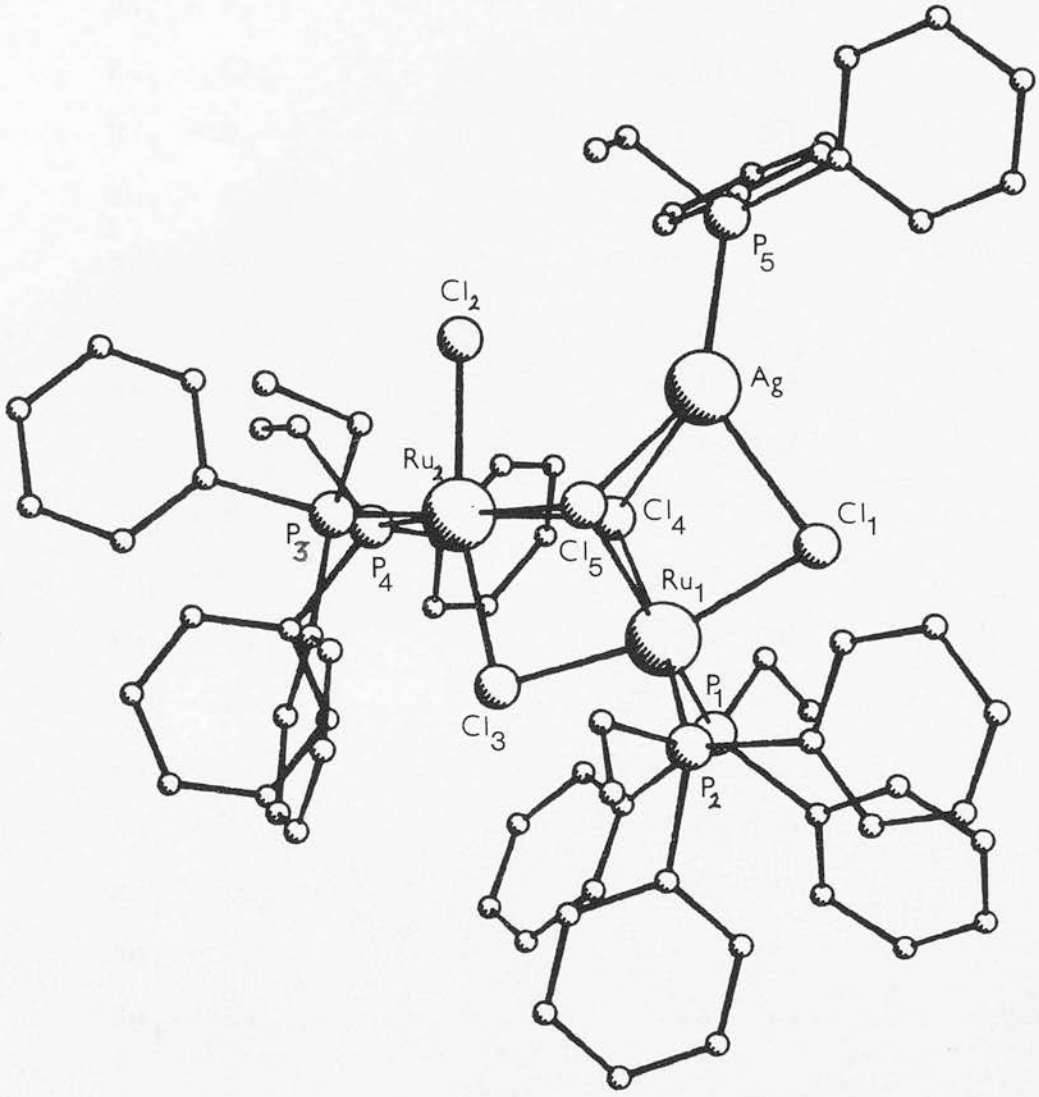


Table 6.1 Bond lengths (Å) with standard deviations for $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ (70)

$Ru_1 - Ru_2$	3.331 (2)
$Ru_1 - P_1$	2.282 (5)
$Ru_1 - Cl_1$	2.433 (6)
$Ru_1 - P_2$	2.280 (6)
$Ru_1 - Cl_5$	2.578 (5)
$Ru_1 - Cl_4$	2.493 (5)
$Ru_1 - Cl_3$	2.378 (5)
$Ru_2 - P_3$	2.274 (6)
$Ru_2 - Cl_2$	2.441 (5)
$Ru_2 - P_4$	2.280 (6)
$Ru_2 - Cl_5$	2.570 (5)
$Ru_2 - Cl_4$	2.490 (5)
$Ru_2 - Cl_3$	2.449 (5)
$Ag_1 - Cl_1$	2.675 (6)
$Ag_1 - Cl_5$	2.657 (5)
$Ag_1 - Cl_4$	2.788 (5)
$Ag_1 - P_5$	2.376 (6)
$Ag_1 \cdots Cl_2$	3.457 (6)

Table 6.2 Bond angles (degrees) with standard deviations for $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ (70)

CL1	RU1	CL4	84.981	0.174
CL1	RU1	CL3	164.084	0.188
P2	RU1	CL5	93.750	0.190
P2	RU1	CL4	170.615	0.196
P2	RU1	CL3	93.085	0.196
CL5	RU1	CL4	77.967	0.160
CL5	RU1	CL3	81.908	0.167
CL4	RU1	CL3	81.480	0.167
RU1	RU2	P3	121.283	0.161
RU1	RU2	CL2	121.391	0.138
RU1	RU2	P4	123.850	0.159
RU1	RU2	CL5	49.787	0.116
RU1	RU2	CL4	48.085	0.115
RU1	RU2	CL3	45.486	0.121
P3	RU2	CL2	91.830	0.200
P3	RU2	P4	98.849	0.215
P3	RU2	CL5	88.705	0.191
P3	RU2	CL4	166.817	0.198
P3	RU2	CL3	96.478	0.196
CL2	RU2	P4	91.742	0.197
CL2	RU2	CL5	89.334	0.172
CL2	RU2	CL4	89.458	0.172
CL2	RU2	CL3	166.876	0.183
P4	RU2	CL5	172.328	0.197
P4	RU2	CL4	94.223	0.189
P4	RU2	CL3	96.975	0.193
CL5	RU2	CL4	78.188	0.161
CL5	RU2	CL3	80.743	0.165
CL4	RU2	CL3	80.162	0.165
CL1	AG1	CL5	80.774	0.165
CL1	AG1	CL4	75.010	0.158
CL1	AG1	P5	136.606	0.201
CL5	AG1	CL4	71.700	0.151
CL5	AG1	P5	136.796	0.196
CL4	AG1	P5	129.223	0.189
RU1	CL1	AG1	86.321	0.175
RU2	RU1	P1	119.389	0.148
RU2	RU1	CL1	116.911	0.141
RU2	RU1	P2	122.978	0.159
RU2	RU1	CL5	49.559	0.116
RU2	RU1	CL4	48.003	0.115
RU2	RU1	CL3	47.256	0.124
P1	RU1	CL1	94.491	0.193
P1	RU1	P2	98.416	0.206
P1	RU1	CL5	167.296	0.187
P1	RU1	CL4	89.610	0.180
P1	RU1	CL3	93.747	0.186
CL1	RU1	P2	99.143	0.202
CL1	RU1	CL5	87.135	0.175
RU1	CL5	RU2	80.654	0.150
RU1	CL5	AG1	83.848	0.153
RU2	CL5	AG1	93.008	0.165
RU1	CL4	RU2	83.912	0.154
RU1	CL4	AG1	82.769	0.145
RU2	CL4	AG1	91.678	0.157
RU1	CL3	RU2	87.258	0.169

Interestingly, compound (70) can also be synthesised in high yield by reaction of either $Ru_2Cl_4(PEtPh_2)_5$ or $[Ru_2Cl_3(PEtPh_2)_6]Cl$ at ambient temperature with equimolar amounts of AgCl. All these reactions clearly involve cleavage of ruthenium-phosphorus bonds and provide some insight into the possible mechanism of formation of (70).

It is envisaged that the reaction of $RuCl_2(PEtPh_2)_3$ and AgCl to give (70) involves initial formation of the neutral complex $Ru_2Cl_4(PEtPh_2)_5$. Previous studies have shown that $RuCl_2(PEtPh_2)_3$ readily undergoes a self-coupling reaction to give this complex in non-polar solvents such as CH_2Cl_2 whereas in polar solvents a mixture of $Ru_2Cl_4(PEtPh_2)_5$ and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ is obtained.[76] After formation of $Ru_2Cl_4(PEtPh_2)_5$ the proposed next step is formal insertion of AgCl into a Ru-$PEtPh_2$ linkage to give (70). This may be assisted by prior association of an AgCl unit with $Ru_2Cl_4(PEtPh_2)_5$ through two of the bridging chloride ligands.

The formation of (70) from $[Ru_2Cl_3(PEtPh_2)_6]Cl$ and AgCl is also envisaged to proceed <u>via</u> initial formation of $Ru_2Cl_4(PEtPh_2)_5$ which arises from abstraction of a $PEtPh_2$ ligand by AgCl to give $Ag(PEtPh_2)Cl$ and incorporation of the chloride counterion into the binuclear unit. The $Ag(PEtPh_2)Cl$ can then react with $Ru_2Cl_4(PEtPh_2)_5$ in a similar fashion to AgCl although in this case free $PEtPh_2$ is generated.

It is interesting to note that formation of (70) from $RuCl_2(PEtPh_2)_3$ and AgCl takes ca. 3 hours whereas with $Ru_2Cl_4(PEtPh_2)_5$ and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ the reaction takes several days. This may be attributed to the formation of the soluble species $Ag(PEtPh_2)Cl$ in the reaction with $RuCl_2(PEtPh_2)_3$, facilitated by the generation of free $PEtPh_2$ on formation of $Ru_2Cl_4(PEtPh_2)_5$. If one mole equivalent of $PEtPh_2$ is added to a MeOH solution of $Ru_2Cl_4(PEtPh_2)_5$ and suspended AgCl the reaction time for formation of (70) is reduced to several hours, in support of this theory. Using the complex $Ag(PEtPh_2)_2Cl$ instead of AgCl similarly reduces the reaction time.

Scheme 6.1 summarises these postulated reaction pathways.

Low temperature $^{31}P-\{^1H\}$ n.m.r. spectral studies on (70) in CD_2Cl_2 are fully consistent with retention of the solid state structure in solution. Thus at 183 K (Figure 6.2) two AB patterns arise for the $PEtPh_2$ ligands attached to ruthenium, one centred at δ50.0 p.p.m. (J_{AB} = 42 Hz, $\Delta\nu_{AB}$ = 58 Hz) and the other at δ48.4 p.p.m. (J_{AB} = 36 Hz, $\Delta\nu_{AB}$ = 284 Hz). Two characteristic doublets centred at δ10.0 p.p.m. from the silver-bound $PEtPh_2$ ligand ($J_{^{109}Ag^{31}P}$ = 771 Hz, $J_{^{107}Ag^{31}P}$ = 669 Hz) are also observed. These data suggest that, as in the solid

Scheme 6.1 Postulated pathways for reactions of ruthenium(II) complexes with Ag(I) in methanol

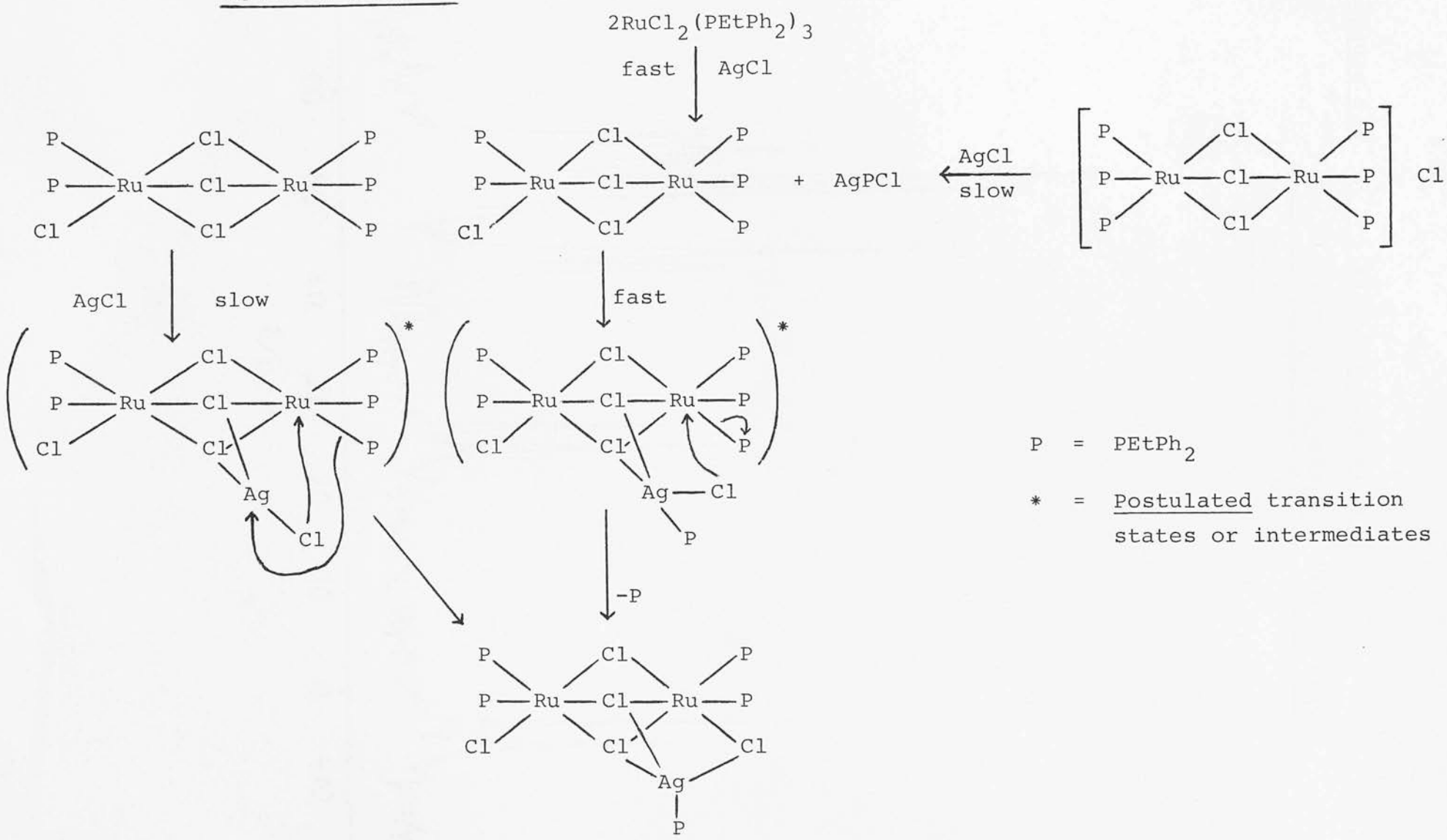
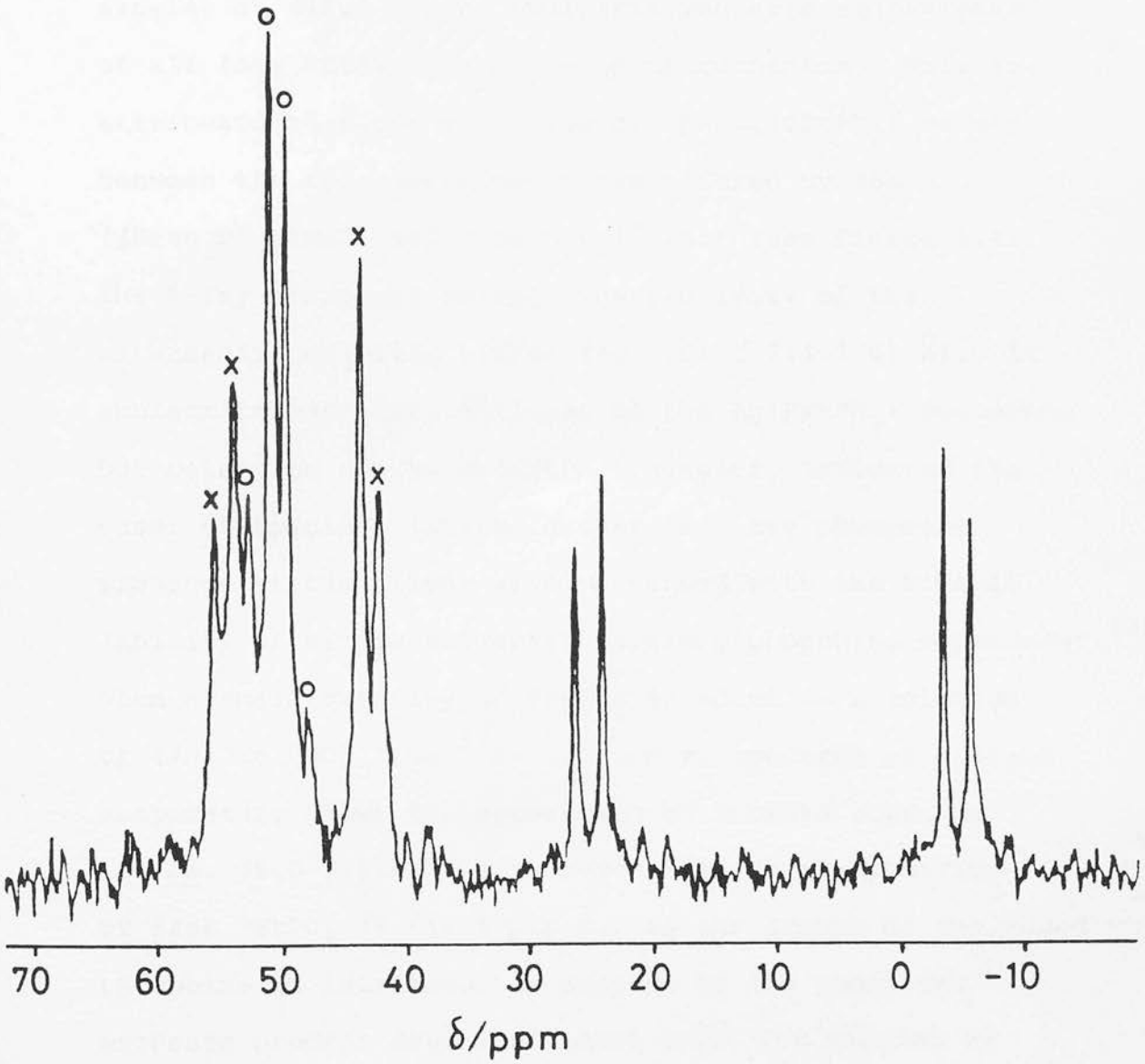


Figure 6.2 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ (70) in CD_2Cl_2 at 183 K.



phase, there is no plane of symmetry relating the two Ru atoms or through the three metal atoms, because of the preferred orientation of the substituents on the $Ag(PEtPh_2)$ moiety. At 223 K (Figure 6.3) a temperature-reversible coalescence of the AB signals to give a singlet at δ48.9 p.p.m. indicates magnetic equivalence of all four $PEtPh_2$ groups bound to ruthenium. This is attributed to ready switching of the $Ag(PEtPh_2)$ moiety between the two equivalent sites offered by the $[(EtPh_2P)_2ClRuCl_3RuCl(PEtPh_2)_2]^-$ unit (see Figure 6.4). The X-ray structure reveals the proximity of the alternative chloride ligand (Ag...Cl , 3.457(6) Å). At ambient temperature, collapse of the $Ag(PEtPh_2)$ resonance but retention of the $Ru(PEtPh_2)$ singlet, indicates the onset of specific intermolecular tertiary phosphine exchange at the silver site (in accord with the kinetic lability of simple silver(I) tertiary phosphine compounds).[129] When a small quantity of $PEtPh_2$ is added to a solution of (70) in $CDCl_3$ the $^{31}P-\{^1H\}$ n.m.r. spectrum at ambient temperature shows the appearance of a broad resonance (at ca. δ6.0 p.p.m.) which moves towards the position of free $PEtPh_2$ (δ -12.5 p.p.m.) as the amount of the added phosphine is increased, in support of the phosphine exchange process described above (n.b. the singlet at δ48.9 p.p.m. is unaffected).

Figure 6.3 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $Ru_2Cl_5(PEtPh)_4.Ag(PEtPh_2)$ (70) in CD_2Cl_2 at 223 K.

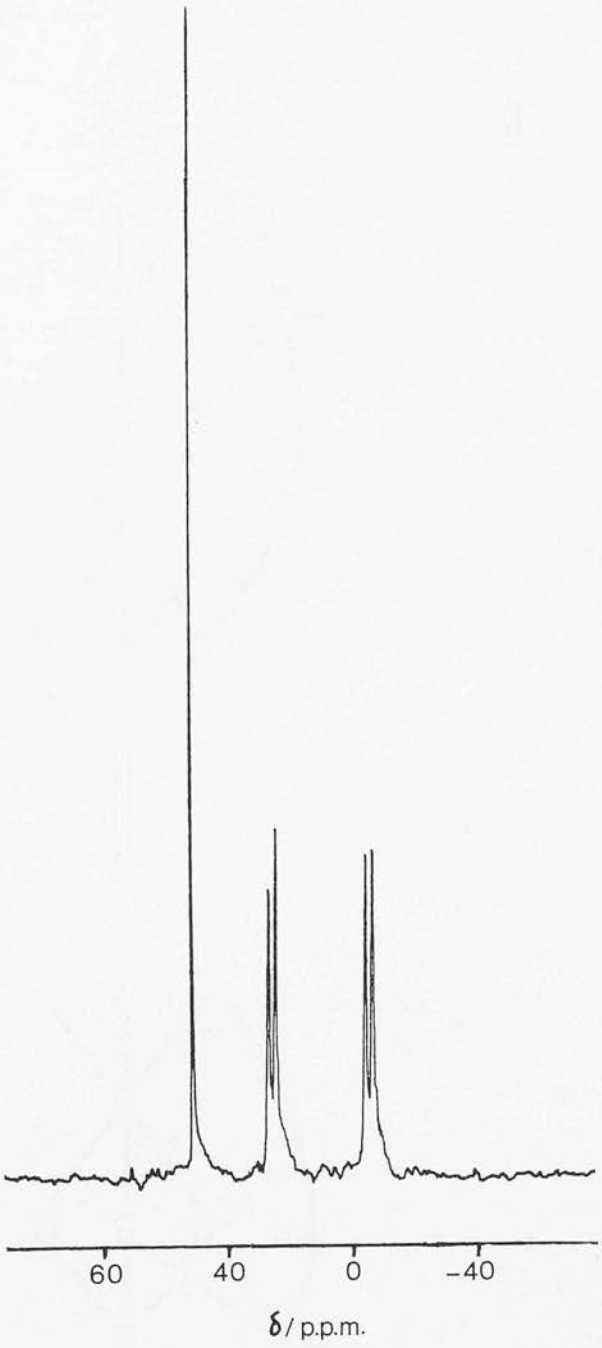
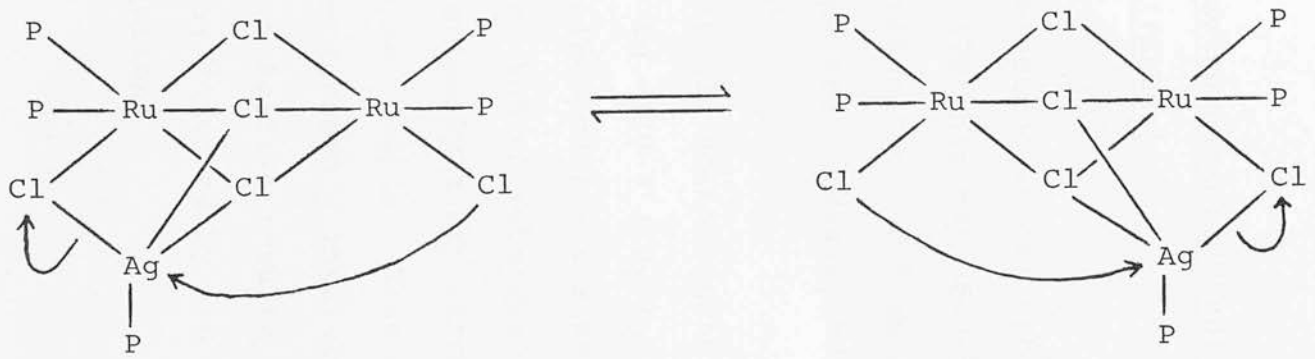


Figure 6.4 Proposed mechanism for fluxional behaviour of $Ru_2Cl_5(PEtPh_2)_4$-$Ag(PEtPh_2)$ in CD_2Cl_2 at ambient temperature



P = $PEtPh_2$

On addition of large quantities of $PEtPh_2$ to a solution of (70) in $CDCl_3$ the $^{31}P-\{^1H\}$ n.m.r. spectrum shows the growth of peaks assigned to the species $RuCl_2(PEtPh_2)_3$, $Ru_2Cl_4(PEtPh_2)_5$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$ and $Ag(PEtPh_2)_2Cl$, due to cleavage of the chloride bridges in (70).

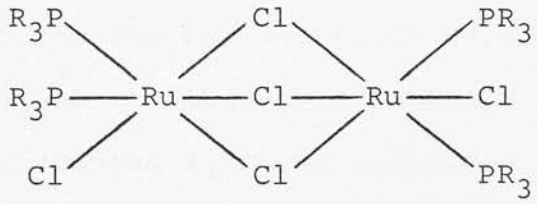
6.2.2 Electrochemical Studies on $Ru_2Cl_5(PEtPh_2)_4 \cdot Ag(PEtPh_2)$

The electrochemical behaviour of $Ru_2Cl_5(PEtPh_2)_4 \cdot Ag(PEtPh_2)$ (70) has been found to be complex, and is not fully understood at the time of writing. Some interesting observations are, however, worth mentioning.

The cyclic voltammogram of the complex in the range -0.2 to +1.0 V (CH_2Cl_2/0.5 M Bu_4NBF_4, Ag/Ag^+ reference electrode) shows several oxidation waves in the initial scan and on subsequent scans additional characteristically sharp strong waves centred on 0.0 V for the Ag/Ag^+ couple. This suggests that oxidation of the complex (probably involving Ru(II) → Ru(III) rather than Ag(I) → Ag(II)) results in displacement of Ag^+, subsequently detected by its characteristic reduction from CH_2Cl_2 solution.

It has also been observed that potentials more negative than -0.35 V cause the appearance of the sharp Ag/Ag^{+} waves on repeated scanning. This is attributed to irreversible loss of the $Ag(PEtPh_2)$ moiety due to direct reduction of the silver(I) centre.

These observations suggest that oxidation of (70) may be a route to the novel mixed-valence complex $Ru_2Cl_5(PEtPh_2)_4$ while reduction of (70) might yield the reduced form of the same complex, i.e. the anion $[Ru_2Cl_5(PEtPh_2)_4]^{-}$. The mixed-valence complex would be particularly interesting since it would be closely related to the "symmetric" complexes $Ru_2Cl_5(PR_3)_4$ (PR_3 = PBu^n_3, $Ppent^n_3$) described by Nicholson which have structure (71) with mutually staggered terminal chloride ligands.[84,85]



(71)

All attempts to prepare these complexes in this department have failed so that a rational route to such systems would be extremely useful.

The hypothetical complex $Ru_2Cl_5(PEtPh_2)_4$ which might be produced on oxidation of (70) differs from Nicholson's complexes in that it would be of higher symmetry, having mutually eclipsed terminal chloride ligands if loss of the $Ag(PEtPh_2)$ moiety occurs without structural change in the binuclear ruthenium unit.

Apart from their innate electronic structural interest, a major incentive to obtaining complexes of the type $Ru_2Cl_5(PR_3)_4$ lies in their possible reactions with $TlBF_4$ in the presence of alkenes and alkynes (cf. Chapter 2).

6.3 Reactions of Other Binuclear Ruthenium(II) Species with AgCl and AgL_2Cl (L = tertiary phosphine)

Treatment of the species $Ru_2Cl_4(PEt_2Ph)_5$, $[Ru_2Cl_3(L)_6]Cl$ (L = PEt_2Ph, PMe_2Ph) and $Ru_2Cl_4(Y)(PPh_3)_4$ (Y = CO, CS) with AgCl in MeOH at ambient temperature results in recovery of the unchanged starting materials.

The failure of these reactions to give species analogous to (70) is attributed to the greater strength of the ruthenium-phosphorus bond for PEt_2Ph and PMe_2Ph compared to $PEtPh_2$, so that insertion of an AgCl unit into this bond is not possible. The lack of reaction of AgCl with the complexes containing PPh_3 ligands, where the ruthenium-phosphorus bond is relatively weak, is attributed to the

bulk of the phosphine which hinders approach of an AgCl unit.

Similar observations are made even when the soluble species AgL_2Cl (L = tertiary phosphine) are used instead of AgCl except that with the complex $Ru_2Cl_4(PEt_2Ph)_5$ the product isolated is $[Ru_2Cl_3(PEt_2Ph)_6]Cl$. This is formed by displacement of terminal chloride by PEt_2Ph which is present in a free state due to the dissociation of $AgCl(PEt_2Ph)_2$.

6.4 Reactions of $RuCl_2(PEtPh_2)_3$ with $Ag(PEtPh_2)_2NO_3$

In order to explore further the reactions of ruthenium(II) tertiary phosphine complexes with silver(I) compounds the reaction between $RuCl_2(PEtPh_2)_3$ and $Ag(PEtPh_2)_2NO_3$ has been studied. Depending on the reaction conditions, either of two novel complexes is obtained as separately described below.

When equimolar amounts of $RuCl_2(PEtPh_2)_3$ and $Ag(PEtPh_2)_2NO_3$ are stirred at ambient temperature in CH_2Cl_2 the colour of the solution rapidly changes (1-2 minutes) from green to red-brown. In the presence of an excess of MeOH this solution deposits light brown crystals over a 24-hour period.

A single crystal X-ray analysis of this complex has shown it to be the chelating nitrato complex $RuCl(O_2NO)(PEtPh_2)_3$ (72) with the structure shown in Figure 6.5. Some selected bond lengths and bond angles are given in Tables 6.3 and 6.4 respectively.

The i.r. spectrum of (72) has bands at 1478 and 1260 cm^{-1} which are assigned to ν_{N-O} and a band at 240 cm^{-1} assigned to ν_{Ru-Cl}.

The $^{31}P-\{^1H\}$ n.m.r. spectrum of (72) in CD_2Cl_2 at ambient temperature consists of a broad resonance at δ42.5 p.p.m. and a smaller broad resonance at δ40.1 p.p.m. On cooling the solution to 253 K (Figure 6.6) these resonances resolve into a well defined A_2B pattern (δ_A 43.0 p.p.m., δ_B 39.6 p.p.m., $\Delta\nu_{AB}$ = 82.0 Hz, J_{AB} = 33.0 Hz), consistent with retention of the solid state structure in solution at this temperature. The broad resonances at ambient temperature are probably due to fluxional behaviour with the nitrato ligand alternating rapidly between mono and bidentate coordination. This type of fluxionality has been previously observed in complexes such as $Ru(CO)_2(NO_3)_2(PPh_3)_2$.[130]

Figure 6.5 Structure of $RuCl(O_2NO)(PEtPh_2)_3$ (72)

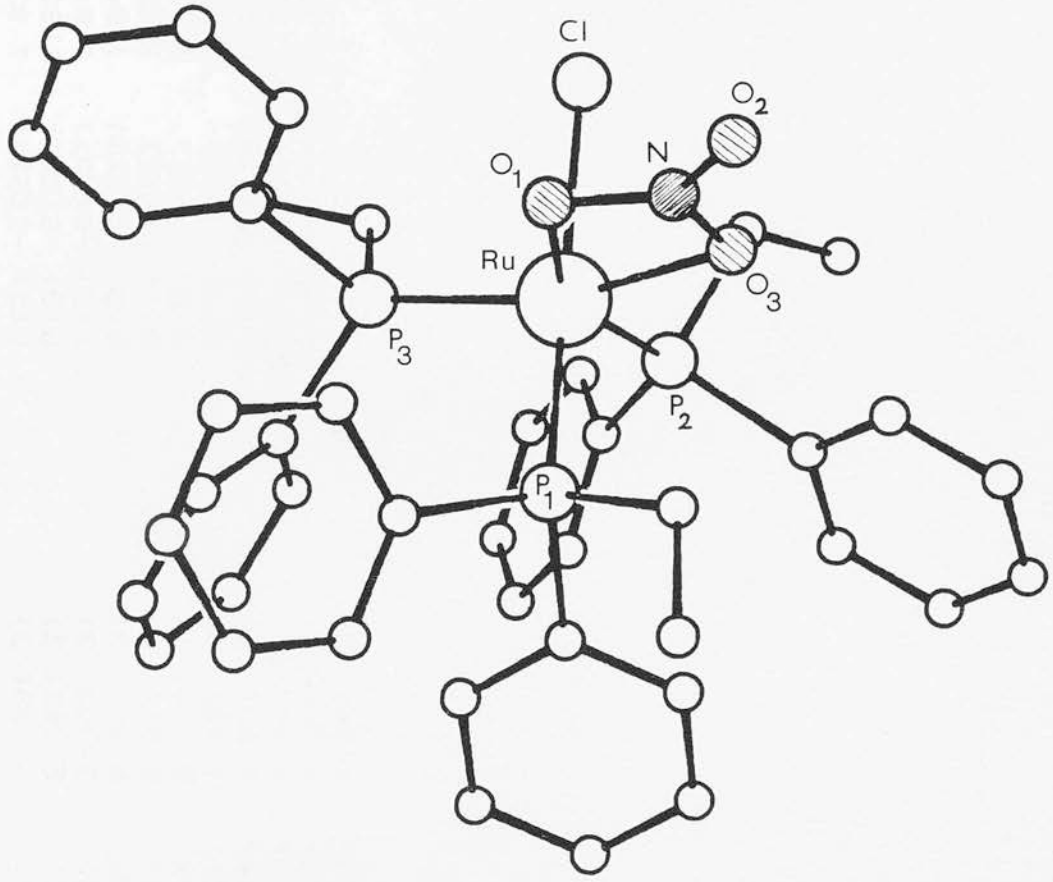


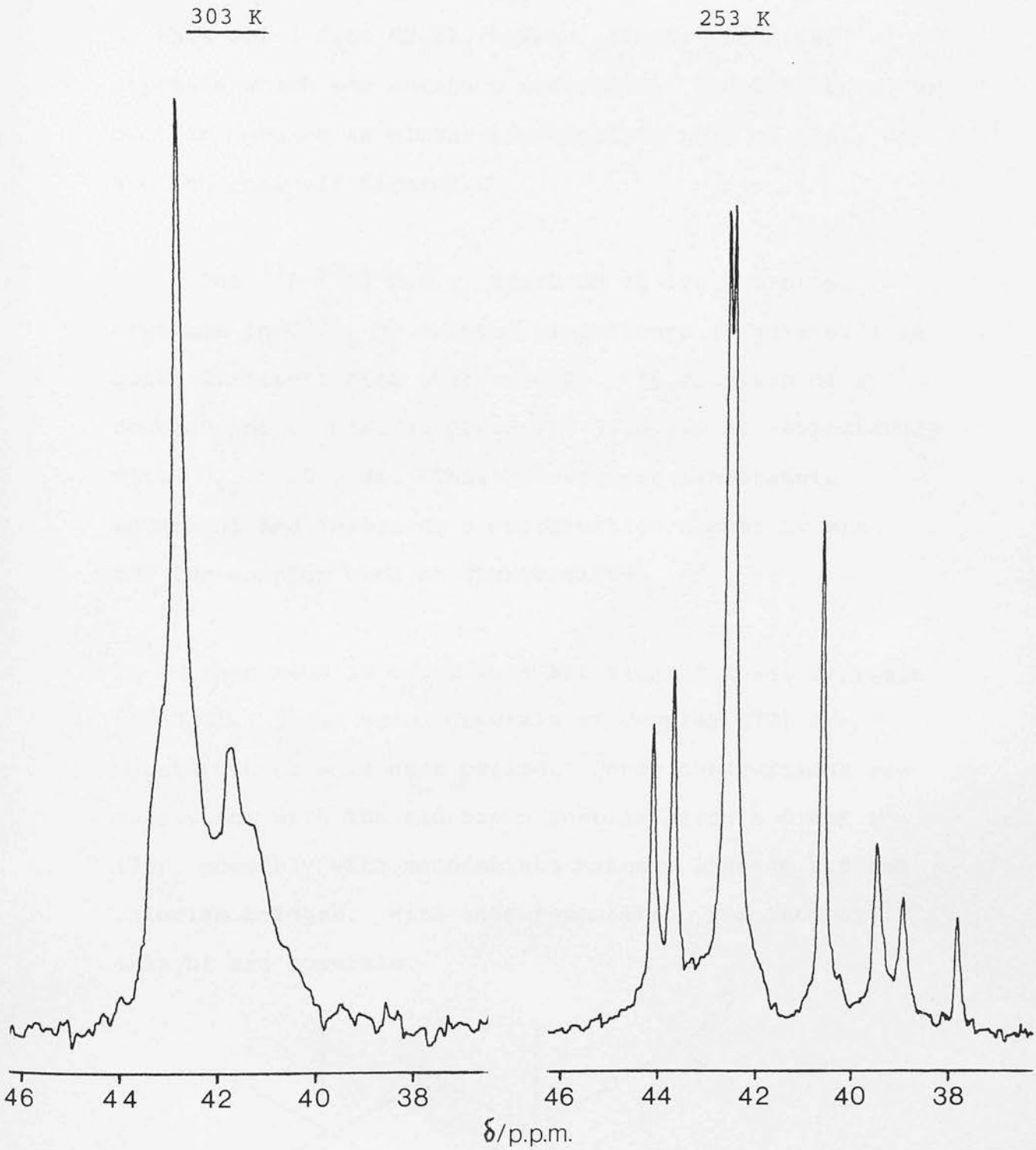
Table 6.3 Bond lengths (Å) with standard deviations for $RuCl(O_2NO)(PEtPh_2)_3$ (72)

Ru(1) -Cl(1)	2.433(3)	P(2) -C(213)	1.833(13)
Ru(1) - P(1)	2.342(3)	P(3) -C(301)	1.851(7)
Ru(1) - P(2)	2.305(3)	P(3) -C(307)	1.849(8)
Ru(1) - P(3)	2.329(3)	P(3) -C(313)	1.846(15)
Ru(1) - O(1)	2.276(7)	O(1) - N(1)	1.281(12)
Ru(1) - O(3)	2.155(7)	O(2) - N(1)	1.218(13)
P(1) -C(101)	1.854(8)	O(3) - N(1)	1.273(12)
P(1) -C(107)	1.831(7)	C(113)-C(114)	1.534(17)
P(1) -C(113)	1.863(12)	C(213)-C(214)	1.525(20)
P(2) -C(201)	1.856(7)	C(313)-C(314)	1.484(22)
P(2) -C(207)	1.841(8)		

Table 6.4 Bond angles (degrees) with standard deviations for $RuCl(O_2NO)(PEtPh_2)_3$ (72)

Cl(1) -Ru(1) - P(1)	166.05(10)	Ru(1) - P(3) -C(301)	112.80(24)
Cl(1) -Ru(1) - P(2)	92.03(10)	Ru(1) - P(3) -C(307)	123.5(3)
Cl(1) -Ru(1) - P(3)	87.49(10)	Ru(1) - P(3) -C(313)	113.3(5)
Cl(1) -Ru(1) - O(1)	79.87(19)	C(301)- P(3) -C(307)	101.1(3)
Cl(1) -Ru(1) - O(3)	81.56(21)	C(301)- P(3) -C(313)	100.3(5)
P(1) -Ru(1) - P(2)	99.57(10)	C(307)- P(3) -C(313)	102.8(5)
P(1) -Ru(1) - P(3)	98.56(10)	Ru(1) - O(1) - N(1)	90.7(6)
P(1) -Ru(1) - O(1)	86.30(19)	Ru(1) - O(3) - N(1)	96.5(6)
P(1) -Ru(1) - O(3)	89.61(21)	O(1) - N(1) - O(2)	122.9(9)
P(2) -Ru(1) - P(3)	97.46(10)	O(1) - N(1) - O(3)	114.6(8)
P(2) -Ru(1) - O(1)	152.85(19)	O(2) - N(1) - O(3)	122.5(9)
P(2) -Ru(1) - O(3)	95.39(21)	P(1) -C(101)-C(102)	116.4(5)
P(3) -Ru(1) - O(1)	107.92(19)	P(1) -C(101)-C(106)	123.5(5)
P(3) -Ru(1) - O(3)	163.39(21)	P(1) -C(107)-C(108)	120.0(5)
O(1) -Ru(1) - O(3)	58.0(3)	P(1) -C(107)-C(112)	120.0(5)
Ru(1) - P(1) -C(101)	114.47(25)	P(1) -C(113)-C(114)	116.6(8)
Ru(1) - P(1) -C(107)	123.50(25)	P(2) -C(201)-C(202)	117.3(5)
Ru(1) - P(1) -C(113)	110.5(4)	P(2) -C(201)-C(206)	122.7(5)
C(101)- P(1) -C(107)	104.0(3)	P(2) -C(207)-C(208)	120.4(5)
C(101)- P(1) -C(113)	99.7(4)	P(2) -C(207)-C(212)	119.6(5)
C(107)- P(1) -C(113)	101.4(4)	P(2) -C(213)-C(214)	117.6(9)
Ru(1) - P(2) -C(201)	114.63(25)	P(3) -C(301)-C(302)	120.1(5)
Ru(1) - P(2) -C(207)	124.4(3)	P(3) -C(301)-C(306)	119.8(5)
Ru(1) - P(2) -C(213)	109.1(4)	P(3) -C(307)-C(308)	120.6(6)
C(201)- P(2) -C(207)	102.9(3)	P(3) -C(307)-C(312)	119.3(6)
C(201)- P(2) -C(213)	97.1(5)	P(3) -C(313)-C(314)	119.4(11)
C(207)- P(2) -C(213)	104.9(5)		

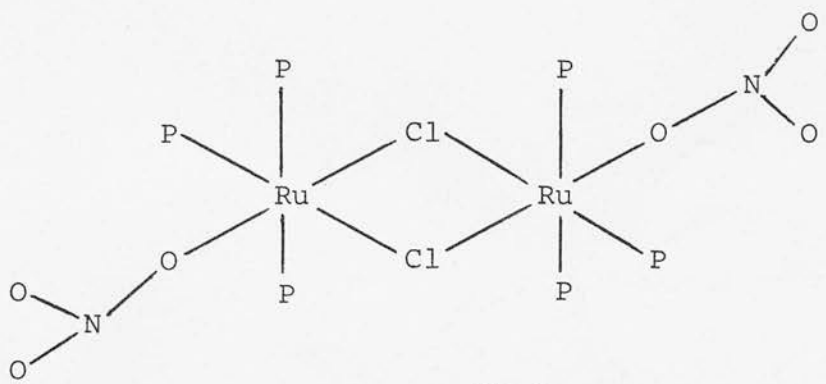
Figure 6.6 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $RuCl(O_2NO)(PEtPh_2)_3$ (72) in CD_2Cl_2



Concentration of the solution obtained on reaction of $RuCl_2(PEtPh_2)_3$ with $Ag(PEtPh_2)_2NO_3$ in CH_2Cl_2, followed by addition of an excess of n-hexane gives a red-brown solid which is non-conducting in CH_2Cl_2. Recrystallisation of this solid from CH_2Cl_2/hexane affords red-brown crystals which are moisture sensitive. The i.r. spectrum of this complex is almost identical to that of (72), as are the analysis figures.

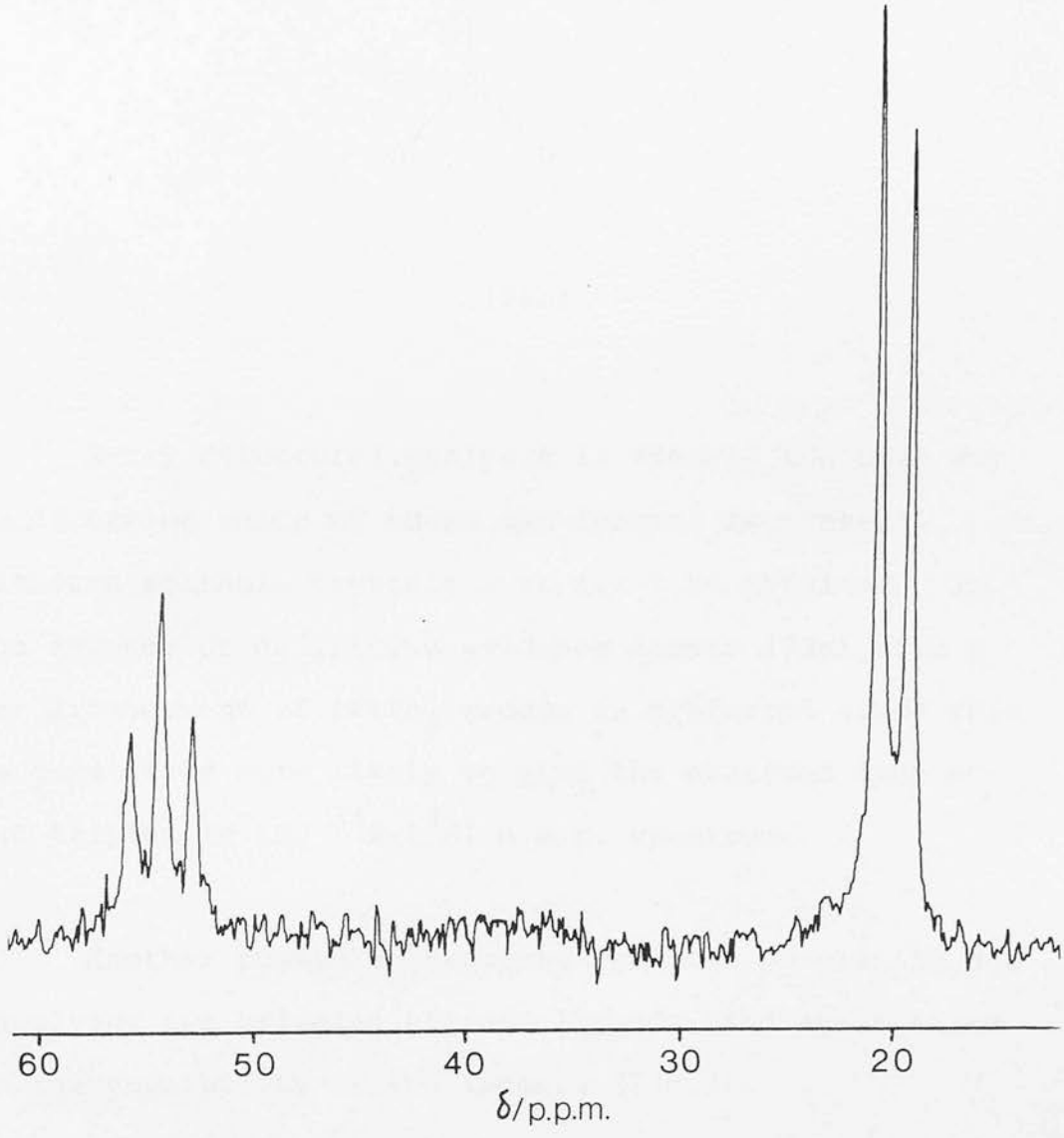
The $^{31}P-\{^1H\}$ n.m.r. spectrum of the red-brown crystals in $CDCl_3$ at ambient temperature (Figure 6.7) is quite different from that of (72). It consists of a doublet and triplet at δ26.5 and 54.8 p.p.m. respectively with $^2J_{PP}$ = 30.3 Hz. This spectrum is temperature invariant and indicates a coordination number of six for the complex with no fluxionality.

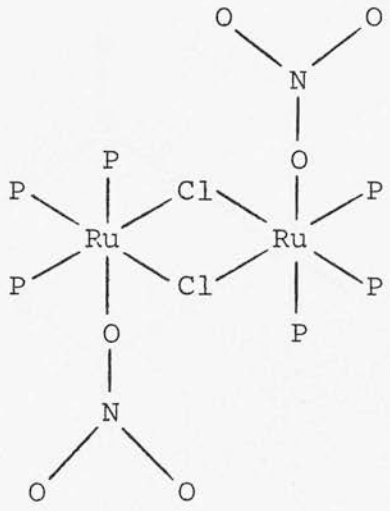
When MeOH is added to a solution of these crystals in CH_2Cl_2, light brown crystals of complex (72) are obtained over a 24 hour period. These observations are consistent with the red-brown complex being a dimer of (72), possibly with monodentate nitrate ligands and two chloride bridges. With this formulation two isomers (73a,b) are possible.



(73a)

Figure 6.7 $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[RuCl(ONO_2)(PEtPh_2)_3]_2$ (73) in $CDCl_3$

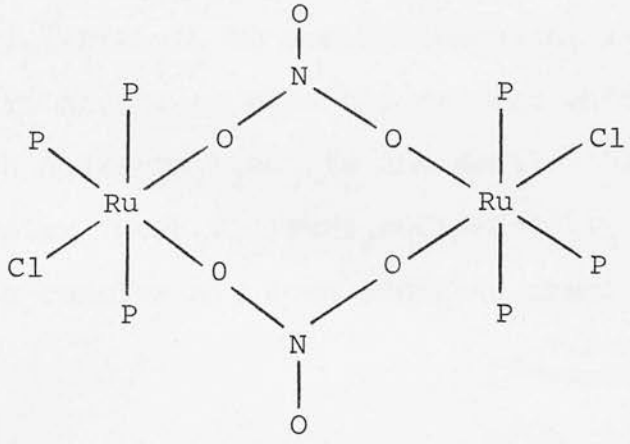




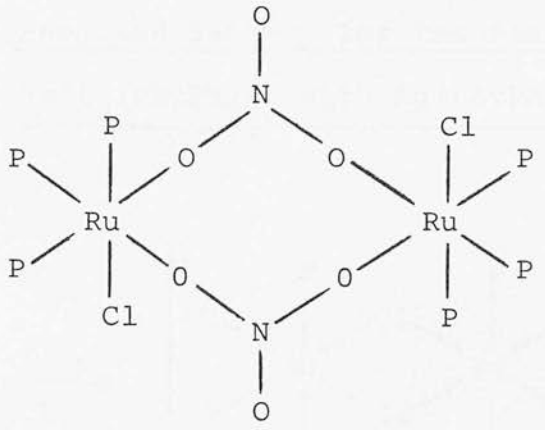
(73b)

X-ray structural analysis is clearly the best way to determine which of these two isomers is present, although suitable crystals must first be obtained. In the absence of definitive evidence isomer (73a) with a mer arrangement of $PEtPh_2$ groups is preferred since this is considered more likely to give the observed doublet and triplet in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum.

Another possible structure for this complex is one involving two bridging nitrate ligands, and again there is the possibility of two isomers (73c,d).



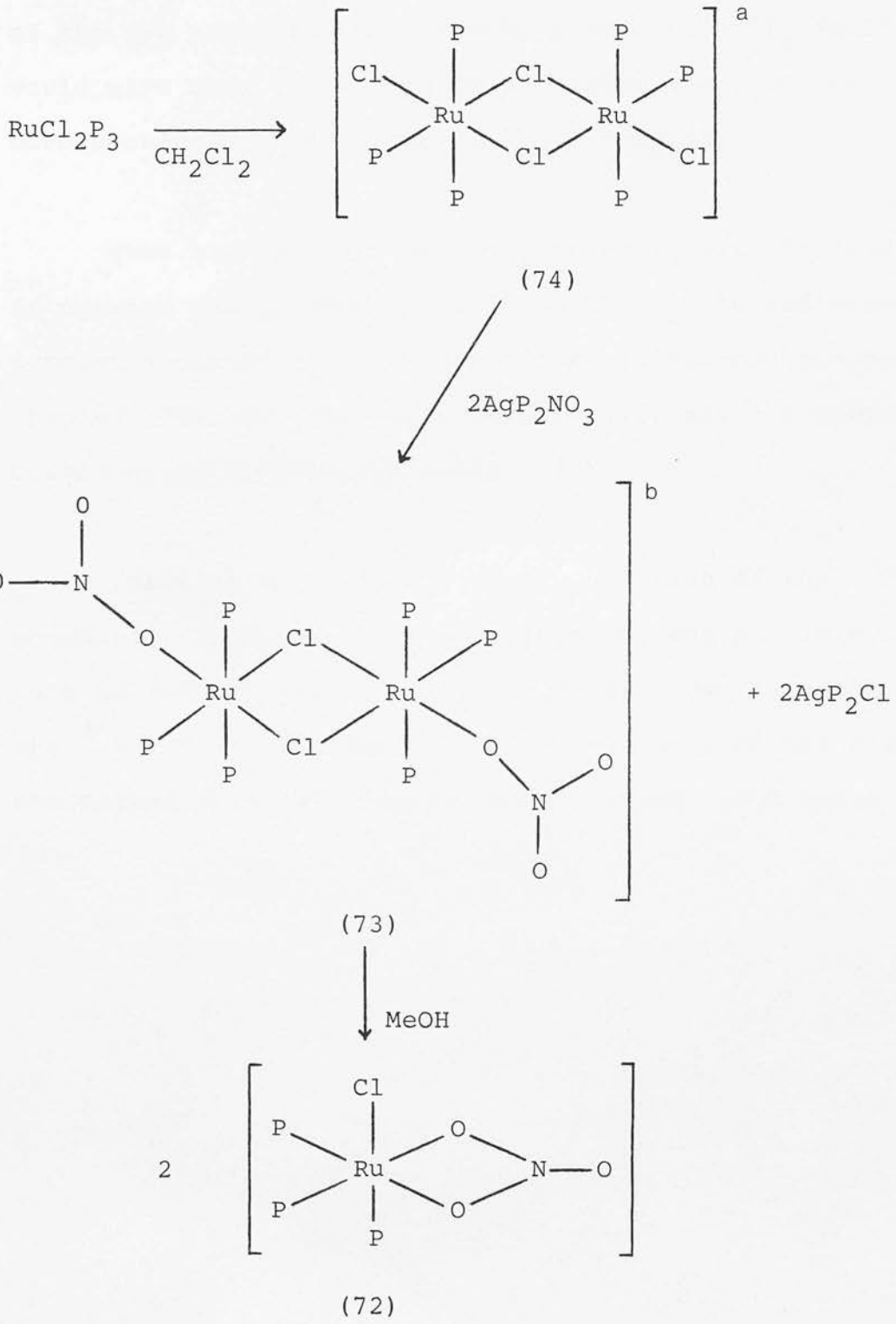
(73c)



(73d)

Though possible, such a structure is considered less likely for the following reasons. All attempts to induce a self-coupling reaction of the monomeric complex (72) to produce (73) have failed. For example, addition of a non-polar solvent such as n-hexane to a CH_2Cl_2 solution of the light brown complex (72) results in the growth of crystals of the unchanged monomeric complex. This occurs even after heating of the solution. The irreversible nature of the observed conversion of the 'dimeric' complex (73) to the monomeric species (72) in the presence of a polar solvent suggests that (73) is the initial product of the reaction between $RuCl_2(PEtPh_2)_3$ and $Ag(PEtPh_2)_2NO_3$. In view of the known tendency of $RuCl_2(PEtPh_2)_3$ to undergo coupling reactions in solution[76] it is envisaged that the species which actually reacts with $Ag(PEtPh_2)_2NO_3$ is the double-chloride-bridged complex $(EtPh_2)_3ClRuCl_2RuCl(PEtPh_2)_3$ (74) (see Scheme 6.2). This complex has been proposed previously as an intermediate

Scheme 6.2 Proposed Pathway for the Reaction of $RuCl_2(PEtPh_2)_3$ with $Ag(PEtPh_2)_2NO_3$



P = $PEtPh_2$

[a] Proposed transition state or intermediate, not observed or isolated.

[b] Isomeric form of this postulated formulation not certain.

in the formation of the triple-chloride-bridged species $Ru_2Cl_4(PEtPh_2)_5$ and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ from $RuCl_2(PEtPh_2)_3$ although it has not been isolated or observed on the n.m.r. time scale.[7b] It is interesting to note that retention of the mer arrangement of $PEtPh_2$ groups in $RuCl_2(PEtPh_2)_3$ would give rise to the preferred isomer (73a) of the double-chloride-bridged bis-nitrato complex.

When the reaction of $RuCl_2(PEtPh_2)_3$ with $Ag(PEtPh_2)_2NO_3$ is carried out in MeOH rather than CH_2Cl_2 the red-brown product isolated is a mixture of the silver-containing complex (70), the monomeric complex (72) and the postulated double-chloride-bridged complex (73).

Interestingly, when a CD_2Cl_2 solution of the monomeric complex (72) in an evacuated, sealed n.m.r. tube is left at ambient temperature for several weeks the $^{31}P-\{^1H\}$ n.m.r. spectrum shows the loss of the signals associated with the complex and the growth of a large peak at δ30.2 p.p.m., attributed to $OPEtPh_2$. The i.r. spectrum of the solution shows the presence of a very intense band at 1840 cm^{-1}, assigned to $\nu_{N\equiv O}$ of a nitrosyl group. Attempts to isolate a solid from such 'aged' solutions of (72) have been unsuccessful. It would appear that transfer of oxygen from the coordinated nitrate ligand to $PEtPh_2$ has occurred. Reactions of this type have been observed previously; for example,

treatment of $RuH_2(CO)(PPh_3)_3$ with 16M HNO_3 gives the complex $Ru(NO_3)_3(NO)(PPh_3)(OPPh_3)$ which contains a nitrosyl and an $OPPh_3$ ligand.[130] It would be interesting to study further the reaction of (72) in order to ascertain whether the transfer of oxygen from nitrate to $PEtPh_2$ involves an intermediate with coordinated dioxygen. The slow rate of the reaction should facilitate such a study.

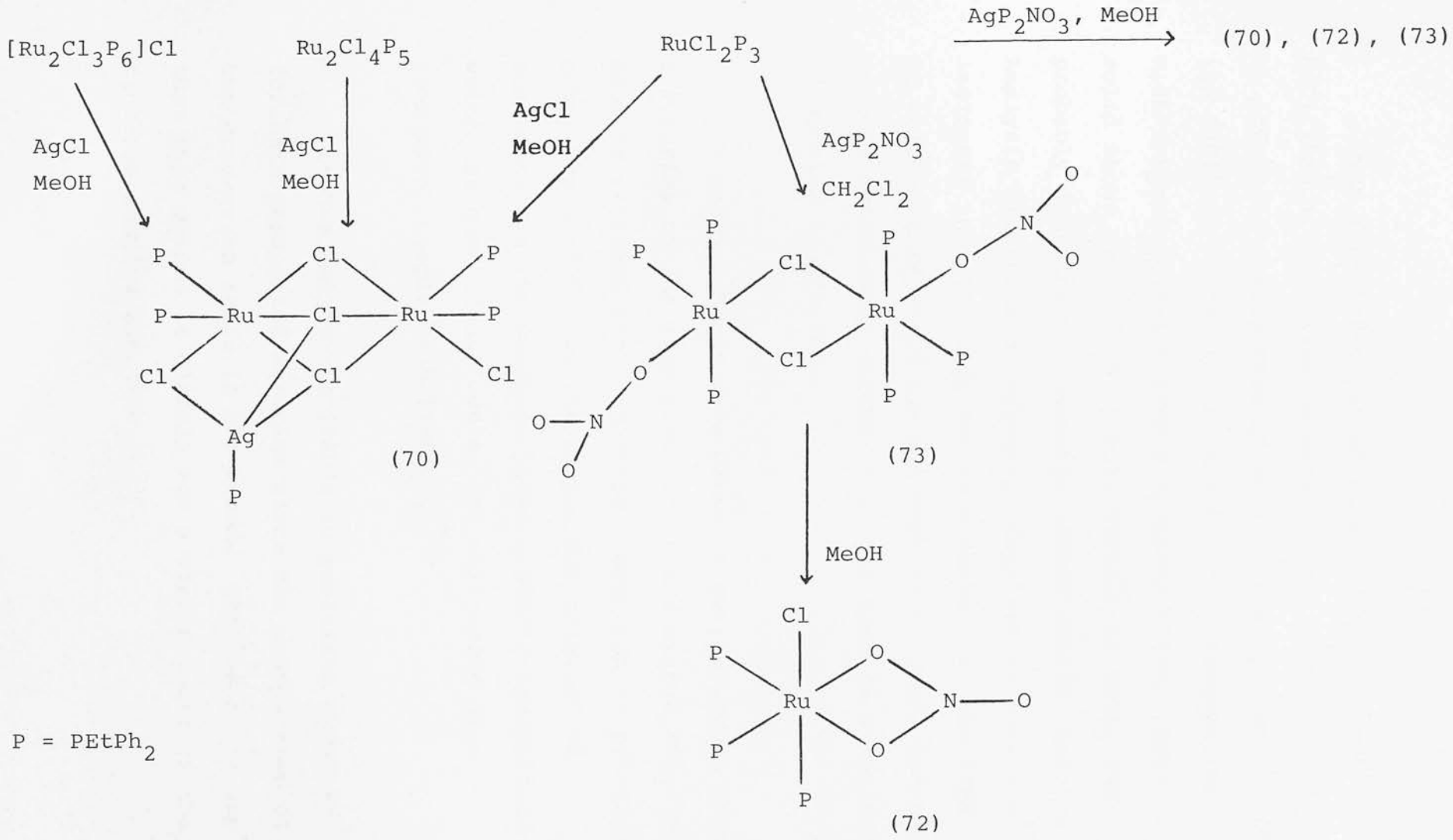
The reactions of monomeric and binuclear ruthenium(II) complexes with silver(I) species are summarised in Scheme 6.3.

Finally, preliminary studies show that $RuCl_2(PEtPh)_3$ reacts readily with other simple metal species such as $PtCl_2$ and $PdCl_2(PhCN)_2$, and there are strong indications that the products isolated are heterometallic in nature.

6.5 Reactions of Ruthenium(II) Complexes in Fluoride Containing Media

The complex $RuCl_2(PPh_3)_3$ has been treated with $Ag_2(CO)_3$ and aqueous HF in MeOH. The aim of the reaction was to generate AgF *in situ* which may then react with $RuCl_2(PPh_3)_3$ to give $RuF_2(PPh_3)_3$ and a precipitate of AgCl (AgF is reasonably soluble in MeOH whereas AgCl is not). Reactions of $RuF_2(PPh_3)_3$ with various tertiary phosphines could then be carried out in attempts to prepare triple-fluoride-bridged binuclear complexes.

Scheme 6.3 Summary of Reactions of Ruthenium(II) Complexes with Silver(I) Species



Over a period of several hours the suspended $RuCl_2(PPh_3)_3$ dissolves to give a green solution and an off-white precipitate of AgCl. After filtering off the AgCl and concentrating the filtrate, trituration with n-hexane gives a dark grey-green solid. This solid shows no $^{31}P-\{^1H\}$ n.m.r. signals in $CDCl_3$ and probably contains paramagnetic ruthenium(III) species. Analysis figures are variable. Qualitative analysis[131] indicates that fluoride ion is present. At the time of writing this solid has not been identified, nor has it been established whether a single species or mixture of species is present.

A colour change from green to purple occurs when a solution of the grey-green solid and excess PPh_3 in MeOH is refluxed for 45 minutes. Addition of petroleum ether (bp 60-80°C) to the purple oil obtained on concentrating the solution gives a purple precipitate which has been identified as the well-known (air sensitive) complex $RuHCl(PPh_3)_3$.[132]

It has not been possible to postulate a pathway for this unexpected reaction since the composition of the grey-green solid is not known. Suffice it to say that this method is clearly not a viable route to the fluoride complex $RuF_2(PPh_3)_3$.

Treatment of $RuCl_2(PPh_3)_3$ with TlF in thf or CH_2Cl_2 gives no observable reaction, whereas a very slow reaction occurs between $Ru_2Cl_4(PEt_2Ph)_5$ and TlF in CH_2Cl_2 at ambient temperature to give $[Ru_2Cl_3(PEt_2Ph)_6]^+$ and $[RuCl_2(PEt_2Ph)_2]_n$. These are the same products as are obtained when $Ru_2Cl_4(PEt_2Ph)_5$ is treated with $TlBF_4$ in CH_2Cl_2 under argon (Chapter 2, Section 2.3.2.1.10). This clearly shows that abstraction of terminal chloride has taken place and that scavenging of PEt_2Ph groups occurs in preference to incorporation of fluoride ion.

Following the method employed by Bruce[128] for the preparation of $RuF(cp)(PPh_3)_2$ the complex $RuCl_2(PPh_3)_3$ was treated with NH_4F in refluxing methanol. After addition of Ag_2CO_3 the solution was filtered into water to give a pale yellow solid. This was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to be a PPh_3 complex of silver(I). The fate of the ruthenium in this reaction is not known.

Finally, when $RuCl_2(PEtPh_2)_3$ is treated with Ag_2CO_3 and aqueous HF in MeOH the previously described heterotrimetallic complex $Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2)$ (70) is obtained, which is where the major work described in this chapter had its origin.

6.6 Conclusions

Despite considerable effort, it has not been found possible to prepare ruthenium(II) complexes containing both tertiary phosphine and fluoride ligands by replacement of chloride with fluoride ions. Such complexes would have had intrinsic merit in the context of possible halide transfer to ruthenium(II)-bound alkene ligands. A better approach may be to start with ruthenium species which already contain fluoride ions. For example, the reaction of $[R_4N]_2RuF_6$ with tertiary phosphines would be of interest.

Although the initial aim of this work has not been achieved it has resulted in the preparation of several interesting compounds. Of greatest interest is the novel heterotrimetallic complex $Ru_2Cl_5(PEtPh_2)_4 \cdot Ag(PEtPh_2)$ (70). Here there exists the unprecedented situation of a triple-chloride-bridged binuclear ruthenium(II) unit behaving as a tridentate ligand, by deploying lone pairs on two bridging and one terminal chloride ligands.

The study of heterometallic complexes has become an area of great activity in recent years and the compound (70) represents a new class of such species. Various heterometallic complexes containing silver(I)

have been described although none of these involve bridging chloride ligands between the two types of metal centre. Thus, $[Ru(CO)_2(dppm)_2.AgCl][AsF_6]_2$ [126] (in which one dppm ligand chelates the ruthenium whilst the other bridges the silver and ruthenium), $(NC)_2Pt(\mu\text{-}dppm)_2AgI$ [133] and $[(RNC)ClM(\mu\text{-}dppm)_2AgCl]X$ (M = Pt, Pd; R = Me, CMe_3, C_6H_4Me-p; X = Cl, BPh_4, PF_6) [134] have been reported. The complexes $L_2M(NCS)_2$-$(NCSAg)_2$ (M = Co(II), Ni(II), Cu(II); L = various ureas, amides and acetanilides) [135] presumably contain bridging NCS groups.

The binuclear ruthenium(II) unit in (70) is itself of a previously unobserved type and preliminary electrochemical studies suggest that oxidation of (70) or reduction of the silver(I) centre results in loss of the $Ag(PEtPh_2)$ moiety. It thus seems likely that the anionic species $[Ru_2Cl_5(PEtPh_2)_4]^-$ and the symmetric mixed-valence complex $Ru_2Cl_5(PEtPh_2)_4$ can be generated either electrochemically or chemically. The latter complex would be of great interest since it is closely related to those prepared by Nicholson, [84,85] which have proved to be elusive in this department.

The complex (70) also seems promising from an organometallic viewpoint. The binuclear ruthenium(II) unit has two terminal chloride ligands so that $TlBF_4$ induced chloride abstraction in the presence of alkenes or

alkynes becomes an obvious area for future work. In addition, the observed lability of the $PEtPh_2$ group attached to the silver centre suggests that replacement of this group by alkenes or alkynes may be possible. The reactivity of alkenes or alkynes coordinated to either a ruthenium(II) or silver(I) centre would be of great interest.

6.7 Experimental Methods

Physical measurements were performed as described in Chapter 2.

Materials

The following were prepared using literature methods: AgL_2Cl (L = $PEtPh_2$, PEt_2Ph, PMe_2Ph, PPh_3),[129] $Ag(PEtPh_2)_2NO_3$,[129] $RuCl_2(PPh_3)_3$,[119] $RuCl_2(PEtPh_2)_3$,[7b] $Ru_2Cl_4L_5$ (L = $PEtPh_2$, PEt_2Ph),[7b] $[Ru_2Cl_3L_6]Cl$ (L = $PEtPh_2$, PEt_2Ph, PMe_2Ph),[7b] $Ru_2Cl_4Y(PPh_3)_4$ (Y = CO, CS).[4a,d]

$Ru_2Cl_5(PEtPh_2)_4.Ag(PEtPh_2).CH_2Cl_2$ (70)

Method (1): $RuCl_2(PEtPh_2)_3$ (0.10 g, 0.12 mmol) and AgCl (0.02 g, 0.13 mmol) were stirred for 3 hours in degassed MeOH (25 cm^3) under N_2. The reddish-brown solid was filtered off and washed with MeOH. The solid was then dissolved in CH_2Cl_2 and the solution filtered to remove excess AgCl. Red crystals of the CH_2Cl_2

solvate were obtained on addition of MeOH. m.p. 152-153°C (0.05 g, 52%).

Found: C, 51.3; H, 4.6; P, 9.3; Cl, 16.1. Calc. for $C_{71}H_{77}Cl_7P_5Ru_2Ag$: C, 51.9; H, 4.7; P, 9.4; Cl, 15.1%.

Mull i.r. spectrum: ν_{Ru-Cl} 320(w), 260(w) cm^{-1}.

Method (2): $Ru_2Cl_4(PEtPh_2)_5$ (0.20 g, 0.14 mmol) and AgCl (0.02 g, 0.16 mmol) were stirred for 3 days in degassed MeOH (25 cm^3) under N_2. The red-pink solid was filtered off, washed with MeOH and recrystallised as above. (0.11 g, 49%).

Method (3): $[Ru_2Cl_3(PEtPh_2)_6]Cl$ (0.30 g, 0.18 mmol) and AgCl were stirred for 3 days in degassed MeOH (25 cm^3) under N_2. The red-pink solid was filtered off, washed with MeOH and recrystallised as above. (0.18 g, 63%).

The reaction times in methods (2) and (3) may be considerably reduced by using $Ag(PEtPh_2)_2Cl$ instead of AgCl.

$RuCl(O_2NO)(PEtPh_2)_3$ (72)

$RuCl_2(PEtPh_2)_3$ (0.30 g, 0.36 mmol) and $Ag(PEtPh_2)_2NO_3$ (0.22 g, 0.37 mmol) were stirred in degassed CH_2Cl_2 (25 cm^3) under N_2 for 30 minutes. The brown solution was filtered to remove a small amount of a fine black solid and the filtrate concentrated to ca. 2 cm^3. Methanol

($25\ cm^3$) was added to the concentrated solution and the product filtered off as light brown crystals after 24 hours. m.p. 142-144°C (0.13 g, 44%).

Found: C, 60.0; H, 5.3; N, 1.6. Calc. for $C_{42}H_{45}ClNO_3P_3Ru$: C, 60.0; H, 5.4; N, 1.7%.

Mull i.r. spectrum: ν_{N-O} 1478(s), 1405(w,sh), 1260(s), ν_{Ru-Cl} 240(w) cm^{-1}.

[RuCl(ONO$_2$)(PEtPh$_2$)$_3$]$_2$.CH$_2$Cl$_2$ (73)

The procedure here was exactly the same as for the monomeric complex (72) described above except that n-hexane was added instead of MeOH at the recrystallisation stage to give red-brown crystals. m.p. 138-141°C (0.15 g, 51%).

Found: C, 57.2; H, 5.1; N, 1.4. Calc. for $C_{85}H_{92}Cl_4N_2O_6P_6Ru_2$: C, 57.8; H, 5.2; N, 1.6%.

The mull i.r. spectrum was virtually identical to that of (72).

The Reaction of RuCl$_2$(PPh$_3$)$_3$ with Ag$_2$CO$_3$ and HF

$RuCl_2(PPh_3)_3$ (0.50 g, 0.52 mmol) and Ag_2CO_3 (0.18 g, 0.65 mmol) were stirred in degassed MeOH ($50\ cm^3$) with 2 drops of 40% aqueous HF solution under N_2 for 3 hours. The green solution was filtered to remove a light grey solid (AgCl) and the filtrate was concentrated in vacuo

to give a green oil. This oil was triturated with n-hexane to give a dark grey-green solid which was filtered off and washed with n-hexane. (0.45 g).

	Found
%C	55.6, 58.1
%H	4.0, 3.8

Qualitative analysis[131] showed the presence of fluoride ion.

The Reaction of the Grey-Green Solid (see above) with PPh_3

0.20 g of the grey-green solid and 0.20 g of PPh_3 were heated in refluxing MeOH (25 cm^3) for 45 minutes. The purple solution (initially green) was filtered to remove a small amount of black material and the filtrate concentrated *in vacuo*. Petroleum ether (b.p. 60-80°C) was added to the purple oil to give an air-sensitive purple solid. (0.18 g). This solid was identified by conventional methods as the known complex $RuHCl(PPh_3)_3$.

APPENDIX I

Abbreviations

acac	acetylacetonate
AcO	acetate
bipy	2,2'-bipyridine
Bu^n	normal butyl
cod	cycloocta-1,5-diene
cot	cyclooctatetraene
cych	cyclohexyl
dmac	dimethylacetylenedicarboxylate
dmf	dimethylformamide
dmso	dimethylsulphoxide
dpae	(1,2-diphenylarsino)ethane
dppm	bis(diphenylphosphino)methane
dppe	(1,2-diphenylphosphino)ethane
Et	ethyl
Hz	Hertz
Me	methyl
m.p.	melting point
n.m.r.	nuclear magnetic resonance
$pent^n$	normal pentyl
Ph	phenyl
p.p.m.	parts per million
Pr^i	iso propyl
Pr^n	normal propyl
py	pyridine
SP	o-styryldiphenylphosphine

trpy	2,2',2''-terpyridine
thf	tetrahydrofuran
p-tol	4-methylphenyl
U.V.	ultra-violet

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Postgraduate Courses Attended

"Pulse Sequences and their Applications to N.M.R. Spectroscopy"

Dr. G.A. Morris, 1983.

"History of the Chemistry Department"

Dr. W.P. Doyle, 1983

"Electrochemistry In and Out of Mothballs"

Dr. G.A. Heath, 1983

"Homogeneous Catalysis"

Dr. T.A. Stephenson, 1983

"Topics in Transition Metal Coordination Chemistry"

Dr. M. Schröder, 1984

"The Use of Microcomputers with Instrumentation"

Dr. A.G. Rowley and Mr. A. King, 1985

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Binuclear Halide-bridged Ruthenium(II) Complexes containing Terminal Alkene, Alkyne, and Dinitrogen Ligands

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Convenient, high-yield routes to the new redox-active complexes $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuL(PEt_2Ph)_2]BF_4$ (L = C_2H_4, PhC≡CH, N_2 *etc.*) and $[(PEt_2Ph)_3ClRu(\mu\text{-}Cl)_2RuL'_2Cl(PEt_2Ph)]$ (L′ = C_2H_4 or PhC≡CH) are described.

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Convenient, high-yield routes to the new redox-active complexes $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuL(PEt_2Ph)_2]BF_4$ (L = C_2H_4, PhC≡CH, N_2 *etc.*) and $[(PEt_2Ph)_3ClRu(\mu\text{-}Cl)_2RuL'_2Cl(PEt_2Ph)]$ (L' = C_2H_4 or PhC≡CH) are described.

A wide range of triple chloride bridged compounds of stoicheiometry $L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}$, (L = soft Lewis base such as PR_3, AsR_3, PF_3, CO, or CS), in oxidation states varying from $Ru_2^{II,II}$ to $Ru_2^{III,III}$ have been synthesised in recent years.[1] Although several monomeric dinitrogen ruthenium complexes are known, the only examples of well defined binuclear species containing terminally bound N_2 appear to be $[Ru_2X_4N_2(PPh_3)_4]$ (X = Cl[2] or H[3]) and $[Ru_2H_6N_2(PPh_3)_4]$.[4]

We now describe a simple, high-yield method of incorporating ligands such as N_2, alkenes, alkynes, *etc.* into the terminal positions of $L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}$ by displacement of terminal chloride using M[BF_4] (M = Ag, Na, or Tl). For example, reaction of $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ in CH_2Cl_2 with equimolar amounts of Tl[BF_4] in the presence of an excess of L at ambient temperature and pressure, (L = N_2, C_2H_4, PhC≡CH, $MeO_2CC{\equiv}CCO_2Me$, MeCN, $MeNO_2$, or PEt_2Ph), produces the cationic complexes $[(PEt_2Ph)_3RuCl_3RuL(PEt_2Ph)_2]BF_4$ in almost quantitative yield.‡

The cyclic voltammogram§ of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (**1**) in CH_2Cl_2 (Scheme 1) shows a reversible one-electron oxidation and a second irreversible oxidation, much like the overall pattern for the analogous ionic dimer $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$ (Scheme 2).[1] The abundant evidence for isolated valencies[1,5] in these binuclear species and the reversible nature of the first wave suggest that the initial oxidation in (**1**) takes place at the $-Ru(PEt_2Ph)_3$ centre.

The N_2 and C_2H_4 compounds are stable in both solid and solution phase at ambient temperature under N_2 and C_2H_4 (1 atm) respectively and can be reversibly interconverted. The N_2 and C_2H_4 ligands are readily replaced by chloride ion to regenerate $[Ru_2Cl_4(PEt_2Ph)_5]$, and by the other ligands L mentioned above to generate $[Ru_2Cl_3L(PEt_2Ph)_5]BF_4$ complexes which are stable under argon.

Under argon, in the absence of other potential ligands, treatment of $[Ru_2Cl_4(PEt_2Ph)_5]$ with M[BF_4] in CH_2Cl_2 leads to formation of $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$ and $[RuCl_2(PEt_2Ph)_2]_n$, presumably *via* attack of a co-ordinatively unsaturated intermediate on unchanged $[Ru_2Cl_4(PEt_2Ph)_5]$.

Finally, reduction of the mixed valence complex $[Ru_2^{II,III}Cl_5(PEt_2Ph)_4]$ with Na[BH_4] in the presence of C_2H_4 or PhC≡CH (L') leads to the unusual bis(alkene) and bis(alkyne) complexes $[(PEt_2Ph)_3ClRu(\mu\text{-}Cl)_2RuL'_2Cl(PEt_2Ph)]$. The asymmetric ligation of these complexes is demonstrated by their ^1H and ^{31}P n.m.r. spectra.

$$[(PEt_2Ph)_3Ru^{II}Cl_3Ru^{II}(C_2H_4)(PEt_2Ph)_2]^+ \quad (36e)$$
(**1**)
$$+1.48\ V \downarrow\uparrow$$
$$[(PEt_2Ph)_3Ru^{III}Cl_3Ru^{II}(C_2H_4)(PEt_2Ph)_2]^{2+} \quad (35e)$$
$$+2.00\ V\P \downarrow$$
$$[(PEt_2Ph)_3Ru^{III}Cl_3Ru^{III}(C_2H_4)(PEt_2Ph)_2]^{3+} \quad (34e)$$

Scheme 1

$$[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^+ \quad (36e)$$
$$+1.20\ V \downarrow\uparrow$$
$$[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{2+} \quad (35e)$$
$$+1.75\ V \downarrow\uparrow$$
$$[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{3+} \quad (34e)$$

Scheme 2

We thank Johnson Matthey plc for loans of '$RuCl_3 \cdot xH_2O$', the S.E.R.C. and I.C.I. plc for financial support (to T. E.), and Drs. W. N. Brooks and C. S. Cundy of I.C.I. New Science Group for useful discussions.

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‡ The complexes have been fully characterised by elemental analyses, and i.r. and n.m.r. (^1H, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$) spectroscopy.

§ $E_{\frac{1}{2}}$ V measured by cyclic voltammetry (scan rate, 0.1 V/s) at 293 K in Bu_4NBF_4–CH_2Cl_2 (0.5 M) *vs.* a Ag/AgI/CH_2Cl_2 reference electrode. $E_{\frac{1}{2}}$ for ferrocene–ferrocinium is 0.60 V in this cell.

¶ Rapid rearrangement observed (no cyclic voltammetric return wave) in the scan rate range 0.05 to 50 V/s, even at 235 K.

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The Preparation of $[Ru_2Cl_5(PEtPh_2)_4{\cdot}Ag(PEtPh_2)]$ by Direct Interaction of Silver(I) Chloride with Triply Chloride Bridged Diruthenium Complexes

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The reaction of $[Ru_2Cl_4(PEtPh_2)_5]$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$, or $[RuCl_2(PEtPh_2)_3]$ with equimolar amounts of AgCl at ambient temperature in methanol gives the novel, fluxional, heterotrimetallic complex $[Ru_2Cl_5(PEtPh_2)_4{\cdot}Ag(PEtPh_2)]$ whose structure has been determined by *X*-ray crystallography and $^{31}P\{^1H\}$ n.m.r. spectroscopy.

The heterotrimetallic complex $[Ru_2Cl_5(PEtPh_2)_4{\cdot}Ag(PEtPh_2)]$ (**1**) is readily prepared in high yield by direct reaction of equimolar amounts of $[Ru_2Cl_4(PEtPh_2)_5]$ and AgCl in methanol at room temperature. Recrystallisation from CH_2Cl_2–MeOH yields red crystals of the dichloromethane solvate, shown by *X*-ray analysis to have the novel structure depicted in Figure 1.† This reveals a formal insertion of AgCl into a Ru–$PEtPh_2$ linkage to produce a four-co-ordinate Ag^I ion linked to one terminal- and two bridging-chloride ligands of the newly formed $[(PEtPh_2)_2ClRu^{II}(\mu\text{-}Cl)_3Ru^{II}Cl(PEtPh_2)_2]^-$ unit. As shown in Figure 1, the co-ordination of the silver atom produces no significant changes in the co-ordination of the two ruthenium atoms.

Interestingly, compound (**1**) can also be synthesised in high yield by reaction of either $[Ru_2Cl_3(PEtPh_2)_6]Cl$ or $[RuCl_2(PEtPh_2)_3]$ at ambient temperature with equimolar amounts of AgCl. Both these reactions clearly involve cleavage of

$$[Ru_2Cl_5(PEtPh_2)_4{\cdot}Ag(PEtPh_2)]$$
(**1**)

ruthenium–phosphorus bonds, probably with the pre-formation of $[Ru_2Cl_4(PEtPh_2)_5]$, whereas, in the absence of AgCl, conversion of $[Ru_2Cl_3(PEtPh_2)_6]Cl$ into $[Ru_2Cl_4(PEtPh_2)_5]$ requires pyrolysis at elevated temperatures.[1]

† *Crystal data* for (**1**) $C_{70}H_{75}AgCl_5P_5Ru_2{\cdot}CH_2Cl_2$, M = 1643.5, monoclinic, space group $P2_1/a$, a = 26.005(5), b = 19.315(6), c = 15.515(3) Å, β = 106.98(1)°, U = 7453(3) Å^3, Z = 4, D_c = 1.40 g cm^{-3}. The structure was based on 3475 data out of 6766 measured to sin θ/λ = 0.48 Å^{-1}; R = 0.060, R_w = 0.070. The structure was solved by Patterson methods. In the refinement, all phenyl rings were constrained to be ideal hexagons, and all hydrogen atoms were held in calculated positions. In the final cycles, 318 parameters were refined, including two positions for a disordered molecule of CH_2Cl_2 solvent of crystallisation. The final electron density map showed no peaks above 0.6 e Å^{-3}. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Variable temperature $^{31}P\{^1H\}$ n.m.r. studies on (**1**) in CD_2Cl_2 are fully consistent with retention of the solid state structure in solution. Thus at 183 K (Figure 2), two AB patterns from the $PEtPh_2$ ligands attached to ruthenium and two characteristic doublets from the $PEtPh_2$ group attached to silver are observed. These spectroscopic data indicate that, as

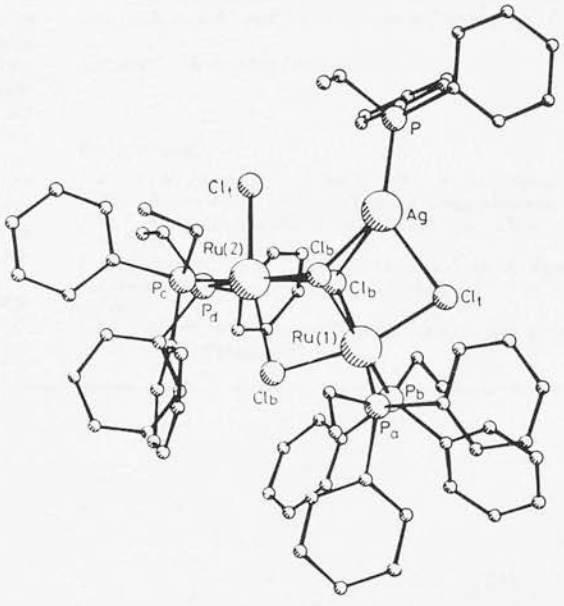


Figure 1. The structure of $[Ru_2Cl_5(PEtPh_2)_4{\cdot}Ag(PEtPh_2)]$ (**1**). Selected bond lengths (Å) (e.s.d.s all 0.006 Å): Ru(1)–P_a 2.280, Ru(1)–P_b 2.282, Ru(1)–Cl_t 2.433, Ru(1)–Cl_b (*trans* to P, attached to Ag) 2.493, 2.578, Ru(1)–Cl_b (*trans* to Cl_t) 2.378, Ru(2)–P_c 2.274, Ru(2)–P_d 2.280, Ru(2)–Cl_t 2.441, Ru(2)–Cl_b (*trans* to P, attached to Ag) 2.499, 2.570, Ru(2)–Cl_b (*trans* to Cl_t) 2.449, Ag–Cl_b 2.657, 2.788, Ag–Cl_t 2.675, Ag · · · Cl_t 3.457, Ag–P 2.376.

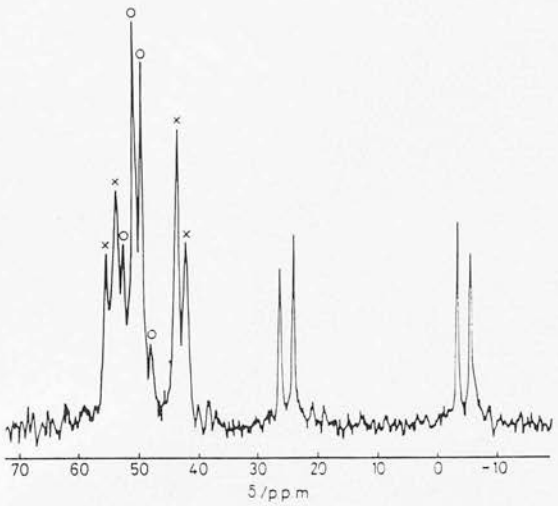
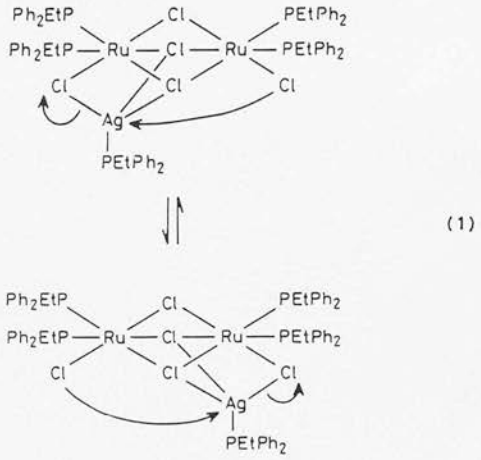


Figure 2. $^{31}P\{^{1}H\}$ n.m.r. spectrum of $[Ru_2Cl_5(PEtPh_2)_4{\cdot}Ag(PEtPh_2)]$ in CD_2Cl_2 at 183 K. Two AB patterns centred at δ 50.0 (○) [$\Delta\nu(P_cP_d)$ 57.9 Hz, $J(P_cP_d)$ 41.9 Hz] and 48.4 (×) [$\Delta\nu(P_aP_b)$ 284.1 Hz, $J(P_aP_b)$ 36.4 Hz] and two doublets centred at 10.0 p.p.m. [$J(^{109}Ag^{31}P)$ 771.5 Hz, $J(^{107}Ag^{31}P)$ 668.9 Hz].

in the solid phase, there is no plane of symmetry relating the two ruthenium atoms, nor through the three metal atoms because of the preferred orientation of the substituents on the $Ag(PEtPh_2)$ moiety. At 223 K, a temperature-reversible coalescence of the AB signals, to give a singlet at δ 48.9 p.p.m., indicates magnetic equivalence of all four $PEtPh_2$ groups bound to ruthenium, and this is attributed to ready switching of the $Ag(PEtPh_2)$ moiety between the two equivalent sites offered by the $[(PEtPh_2)_2ClRu(\mu\text{-}Cl)_3RuCl(PEtPh_2)_2]^-$ unit [see equation (1)]. The *X*-ray structure reveals the proximity of the alternative chloride ligand [Ag · · · Cl_t, 3.457(6) Å]. At ambient temperature, collapse of the $Ag(PEtPh_2)$ resonance but retention of the $Ru(PEtPh_2)$ singlet, indicates the onset of specific intermolecular tertiary phosphine exchange at the silver site [*cf.* the kinetic lability of simple silver(I) tertiary phosphine compounds].[2]

Whereas the asymmetrically ligated $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuCl_2(PEt_2Ph)]^-$ anion is readily prepared by electroreduction of $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuCl_2(PEt_2Ph)]$,[3,4] the



(1)

symmetric $[(PEtPh_2)_2ClRu(\mu\text{-}Cl)_3RuCl(PEtPh_2)_2]^-$ anion represents a new structural category among triply chloride bridged diruthenium compounds. Such distinctions substantially determine mixed valency behaviour.[4]

Cyclic voltammetric studies establish that upon reduction of (**1**), silver metal is released and experiments are now in progress to generate $[(PEtPh_2)_2ClRu(\mu\text{-}Cl)_3RuCl(PEtPh_2)_2]^{-/0}$ species on a preparative scale.

Finally, preliminary studies indicate that $[Ru_2Cl_4(PEtPh_2)_5]$ and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ will react with other metal compounds such as AuCl, CuCl, $PtCl_2$, and $PdCl_2$.

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